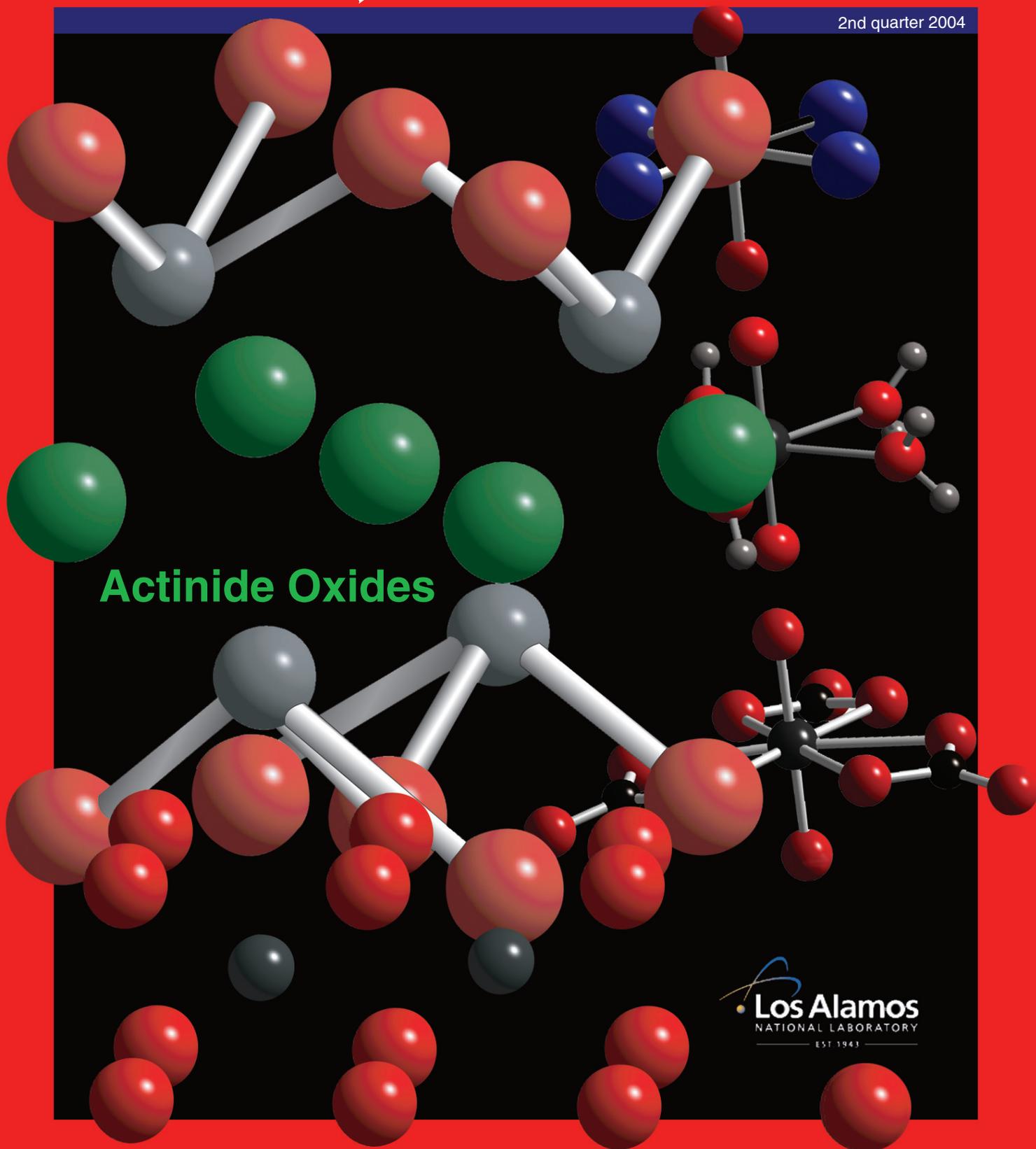


Los Alamos National Laboratory
**ACTINIDE RESEARCH
QUARTERLY**

2nd quarter 2004



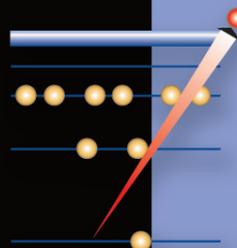
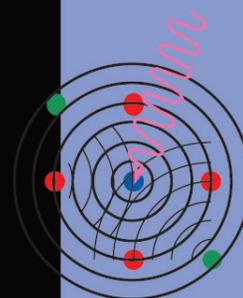
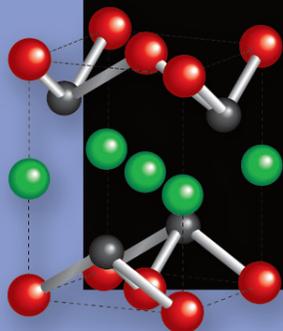
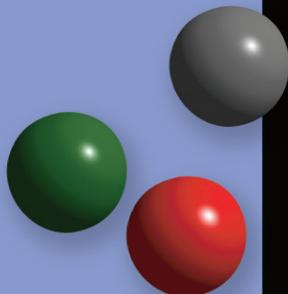
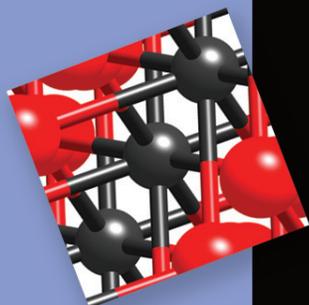
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Nuclear Materials Research and Technology

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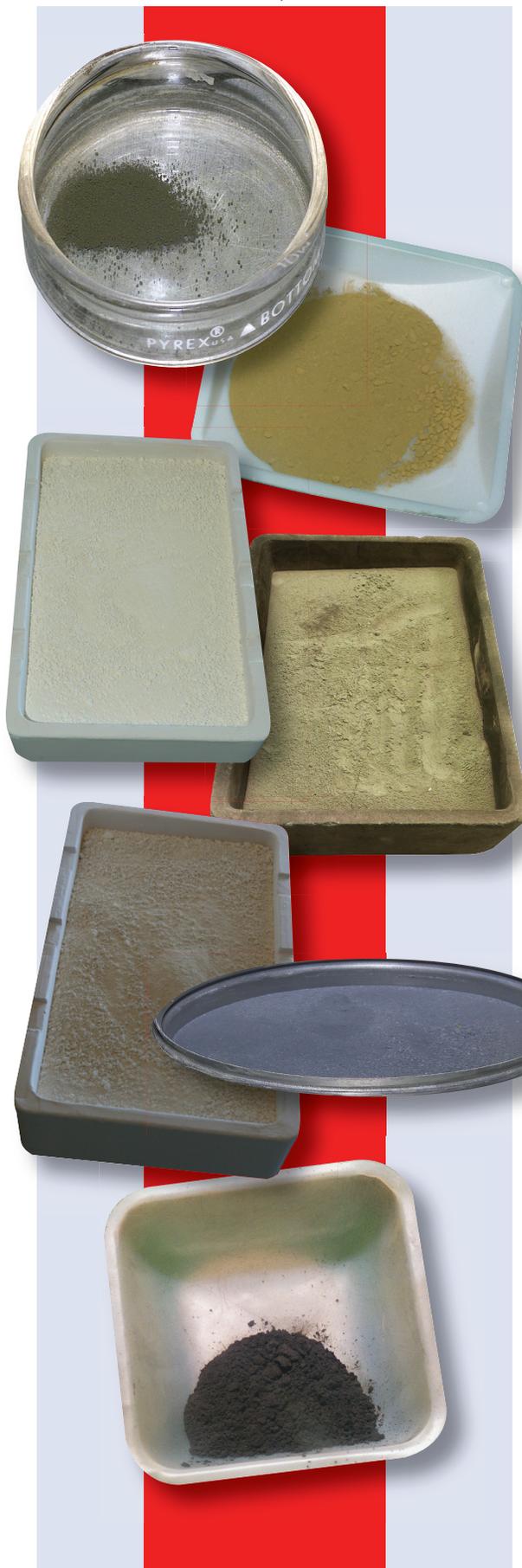
Actinide oxides: exploring their structure, bonding, and reactivity

Understanding the structure, properties, and reactivity of actinide oxides is central to our ability to properly use actinide materials, whether in fabricating nuclear fuel elements, processing materials for long-term storage, or ensuring the integrity of nuclear weapons in the stockpile. This issue of *Actinide Research Quarterly* (and the upcoming 3rd quarter issue) addresses these topics and represents a distillation of a series of talks given at a January 2004 Seaborg Institute workshop titled “Actinide Oxides in the Environment, as Stored Material for Nuclear Fuel Fabrication, and in Practical Weapons Components.”

This issue of ARQ focuses on the structure, bonding, and reactivity of plutonium dioxide (PuO_2) and oxides derived from reactions of this material. The role of lattice oxygen and structural implications in regard to reactivity of the hypervalent PuO_{2+x} (PuO_2 with additional oxygen atoms in the host lattice) have been of considerable debate in recent scientific literature.

The issue begins with an account by Luis Morales of the inherent thermal reactivity of plutonium dioxide with water. This unique—in fact at times perverse—behavior has frequently been attributed to the intrinsic radioactivity that this heavy element possesses. This thermal reactivity, when coupled with radiation-driven chemistry, is an emerging important contributor to actinide-oxide material performance and behavior. From investigations initially begun at Rocky Flats in Colorado and conducted later here at Los Alamos, preliminary suggestions regarding the nature and bonding of the hypervalent PuO_{2+x} were put forth. More recently, other views have emerged based on new data and theoretical considerations.

In the second article, Los Alamos actinide pioneer Robert Penneman provides an alternative view of the structure, bonding, and valence of PuO_{2+x} . The article describes the enormous contributions that Los Alamos workers and collaborators made in unraveling the mysteries of bulk and surface actinide oxides. More importantly, the Zachariasen rules for structural bonding relationships in the actinide oxides and fluorides are discussed and used to describe the local order and bonding in the PuO_{2+x} entity. The predominant motivation for many early studies was simply to understand the structure and bonding in actinide oxides and fluorides. The structure-property relationships of PuO_{2+x} and other actinide oxides of similar stoichiometry are topical, controversial, and significant in the context of understanding the behavior of this material and its congeners when processed and stored.



Additional data have been gathered using modern techniques that complement structural determination data of hypervalent PuO_{2+x} . The new technologies include extended x-ray absorption fine structure (EXAFS) analysis and x-ray photoelectron spectroscopy (XPS).

EXAFS provides information on the local order and structure regularity and is discussed in a third article by a frequent contributor to *ARQ*, Steven Conradson. This information, coupled with other available experimental evidence concerning the nature of the chemical bonding in PuO_{2+x} , presents a picture that is significantly more complex than originally imagined—and at considerable odds with previously postulated structures and stoichiometries.

In the final article, Doug Farr, Roland Schulze, and Mary Neu address the role of the actinide-oxide surface in directing the thermal and radiation-driven reactivity using XPS. Their contribution paints a picture that contrasts with previously postulated structural elements and stoichiometry of PuO_{2+x} . Their article also highlights the importance of other coordination stoichiometries in addressing plutonium-dioxide reactivity with water.

This issue of *ARQ* presents results of studies that tackle the technical detail that has been obscured by lore and an incomplete understanding of the unique complex structure and properties of PuO_{2+x} . The next issue of *ARQ* will provide pragmatic examples of where these factors come into play and justify why and how a strong technical basis ensures the safety and proper stewardship of actinide oxide materials.

—Mark Paffett

Will the real PuO_2 please step forward?

These photos show a wide variability in color and general appearance for samples of plutonium dioxide (PuO_2). This variability in the appearance of PuO_2 samples is well known, and while PuO_2 is normally olive green, samples of yellow, buff, khaki, tan, slate, and black are also common. It is generally believed that the color is a function of chemical purity, stoichiometry, particle size, and method of preparation—although the color of PuO_2 resulting from a given method of preparation is not always reproducible.

Photos by Mick Greenbank and Joe Riedel, NMT-3

*Fifty years of investigation***The path to PuO_{2+x}**

Nearly fifty years ago, J. Drummond and G. Welch reported the first preparations of plutonium dioxides from plutonium (III), (IV), and (VI) compounds by thermal decomposition of the hydride, nitride, carbide, oxalate, sulfate, chloride, fluoride, iodate, hydroxide, and nitrate. They reported apparent oxygen stoichiometries (the oxygen:plutonium ratio) that ranged from 2.04 to 2.09. These results were confirmed at the then-called Los Alamos Scientific Laboratory by G. Waterbury and others and later at Rocky Flats in Colorado by J. Moseley and R. Wing using thermogravimetric techniques.

In each case x-ray diffraction was performed on the oxide products to determine the change in lattice constant with oxygen:plutonium ratio. The x-ray analyses were insensitive to the small differences in the ratios observed in the various oxides. However, several researchers reported that the diffraction lines were broadened, and they also documented the descriptive chemistry of plutonium dioxide via the differing colors obtained from various starting materials and preparative methods (see photos on Page 2).

In contrast, the earliest work on plutonium oxides reported the existence of a monoxide (PuO), a sesquioxide (Pu_2O_3), and a dioxide (PuO_2). The dioxide was found to be the highest-valent oxide based on W.H. Zachariasen's x-ray diffraction work (see Page 9), which showed a fluorite-type face-centered cubic (fcc) structure with a lattice constant of 5.396 angstroms (\AA). E. Westrum Jr. found that the dioxide did not react further with high-pressure oxygen at 400 degrees Celsius or with ozone at 800 degrees Celsius; furthermore, J. Katz and D. Gruen showed that plutonium dioxide was similarly resistant to further oxidation by nitrogen dioxide.

Additional thermogravimetric studies by J. Stakebake and M. Dringman suggested that adsorbed oxygen might be playing a role in weight gains or losses. Furthermore, E. Jackson and M. Rand excluded interstitial lattice oxygen insertion from consideration on the basis of density measurements from plutonium dioxide solids (the expansion of the crystalline lattice was not considered).

At the time, x-ray diffraction techniques were limited in their ability to detect slight changes in the oxygen:plutonium ratio, and it was also difficult to quantify and interpret the line broadening in the powder-diffraction photographs. Thermodynamic calculations, compiled by L. Brewer, revealed plutonium dioxide as the most stable phase in the plutonium-oxygen system and thus the continual quest for plutonium oxides higher than PuO_2 was abandoned by the early 1970s.

However, a 1964 publication by K. Bagnall and J. Laidler, which contradicted the earlier Westrum study, noted that oxidation of plutonium(IV) hydroxide with ozone yielded $\text{PuO}_3 \cdot 0.8\text{H}_2\text{O}$. The presence of plutonium(VI) was shown with ultraviolet-visible (UV-vis)

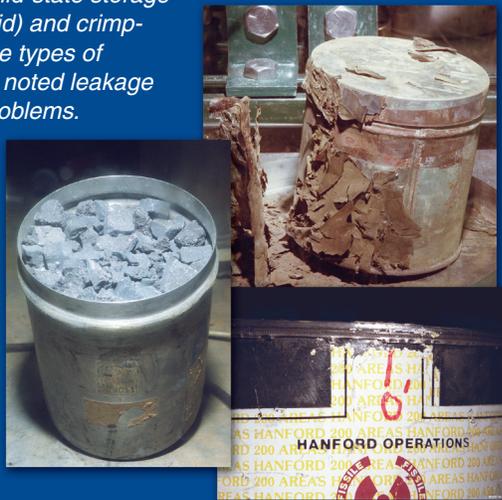
This article was contributed by Luis Morales of the Nuclear Materials Technology Division.

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spectroscopy, but x-ray diffraction data were compromised by the inability to obtain well-crystallized samples. Despite this singular observation of higher-valent plutonium, by the late 1980s the crystallography and the thermodynamics of the plutonium-oxygen system were well established with acceptance of the published plutonium-oxygen phase diagram. However, the descriptive chemistry of plutonium oxide continually revealed anomalies, such as the large variation in the solubility of PuO_2 (10^3 variance) reported by various researchers.

The Bagnall and Laidler report, coupled with renewed interest in actinide-oxide behavior concerning migration in the environment, processing actinide materials for long-term storage, and pragmatic aspects of plutonium corrosion, sparked a resurgent interest in actinide research. These various drivers yielded several interesting developments. The first was in 1993 when Stakebake, D. Larson, and J. Haschke reported that the reaction of plutonium metal with water vapor gave a higher oxide formed at the gas-solid interface with a fluorite structure and contained hexavalent plutonium.

Plutonium-bearing solid-state storage in convenience (slip-lid) and crimp-seal containers. These types of storage vessels have noted leakage and contamination problems.



The second finding came in 1997 when O. Krikorian and coworkers reported that the dependence of the transpiration rate of plutonium on the oxygen pressure at high temperature could only be explained by the presence of PuO_3 in the vapor phase. Additional mass spectroscopic studies monitoring PuO_3 vapor in equilibrium above PuO_2 by C. Ronchi and others in 2000 also revealed the possibility of preparing plutonium oxides with a valence state above (IV).

Independent of these research findings the Defense Nuclear Facilities Safety Board issued findings and recommendations following an incident investigation in which a worker was contaminated while handling a standard storage package (containing 2.5 kilograms of plutonium metal) that developed a breach as a result of radiolysis-driven decomposition of the packaging.

Partially as a result of the desire to ensure the safety of actinide workers, a new plutonium processing, packaging, and storage standard was developed. The DOE 3013 standard (in a number of versions) requires thermal stabilization of oxide materials prior to packaging (without the use of plastics) for storage. A full description of the standard and the fundamental understanding that underpins our technical basis for these procedures will be discussed in the next issue of ARQ.

The DOE 3013 standard states that the plutonium content of processed excess plutonium solids can vary from 88 weight percent (essentially pure PuO_2) to about 30 weight percent. With such a range of composition, the plutonium-bearing solid can be in contact with a variety of other materials. Typically, these “impurities” include alkali metal chlorides, magnesium chloride (MgCl_2), calcium chloride (CaCl_2), magnesium oxide (MgO), ferric oxide (Fe_2O_3), and other materials that are not well characterized. In addition, these solid mixtures come into contact with atmospheric conditions

Cutaway and exterior views of nested, welded 3013 containers for long-term storage of plutonium-bearing solids.



where the moisture content may not be known or well controlled prior to packaging. Therefore, in the areas of excess plutonium disposition and storage, the issue of water and other small molecule interactions with pure or impure plutonium oxide materials and metal remains a continual concern.

Before the DOE 3013 standard, incomplete process control over small molecule reactions in these types of systems led to changes in materials stoichiometry, containment breaches, and dispersal of material resulting from pressurization, corrosion of the container, and collapse of sealed containers because of the formation of partial vacuum. The exact nature of these reactions and the resulting storage implications were not entirely understood, although there had been studies that attempted to explain a large body of experimental

observations. Some of these additional studies will also be described in the next issue of ARQ.

To provide a stronger technical basis for the new storage standard and explain the nature of these small-molecule reactions with plutonium metal and dioxide, we became involved in actinide research in 1995 with a follow-on study of the 1993 Stakebake results by investigating the interaction of plutonium dioxide powders with water from 373 to 623 kelvin (K). A suite of experimental techniques was used that included thermogravimetric analysis—some coupled to mass spectrometry, pressure-volume-temperature (PVT) methods, and x-ray and neutron diffraction of the processed solids. Reaction rates and oxide compositions were determined from changes in sample mass or pressure versus time. Gaseous and solid products were analyzed using mass spectrometry and diffraction methods, respectively. Oxide products have also been characterized by x-ray photoelectron spectroscopy (XPS) and are further discussed in the final article of this issue.

The plutonium-oxide specimens used in our studies were formed by oxidation of electrorefined alpha-phase metal containing approximately 100 parts per million americium as the major metallic impurity. The specific surface area of the oxide was 4.8 square meters per gram. The initial oxide stoichiometry was determined to be $\text{PuO}_{1.97}$ based on the measured lattice parameter and data from the correlation of the cubic lattice parameter (a_0) at fixed oxygen:plutonium ratios with temperature reported by E. Gardner and others.

The reactivity of plutonium dioxide with water was examined using PVT and microbalance measurements at temperatures ranging from 473 to 623 K. These PVT and microbalance results show linear increases in pressure and mass as a function of time. This behavior indicates that water is irreversibly reacting

Further reading

O.J. Wick, editor, *Plutonium Handbook. A Guide to the Technology*, American Nuclear Society, LaGrange Park, Ill., 1980.

J.J. Katz, G.T. Seaborg, and L.R. Morss, editors, *The Chemistry of the Actinide Elements*, 2nd edition, Chapman and Hall, New York, 1986.

H. Wriedt, "The O-Pu (Oxygen-Plutonium) System," *Bulletin of Alloy Phase Diagrams*, **11**, No. 2, 184, 1990.

J. Stakebake, D. Larson, and J. Haschke, "Characterization of the Plutonium-Water Reaction II: Formation of a Binary Oxide Containing Pu(VI)," *Journal of Alloys and Compounds*, **202**, 251, 1993.

O. Krikorian, A. Fontes, B. Ebbinghaus, and M. Adamson, "Transpiration Studies on the Volatilities of $\text{PuO}_3(\text{g})$ and $\text{PuO}_2(\text{OH})_2(\text{g})$ from $\text{PuO}_2(\text{s})$ in the Presence of Steam and Oxygen and Application to Plutonium Volatility in Mixed-Waste Thermal Oxidation Processors," *Journal of Nuclear Materials*, **247**, 161, 1997.

C. Ronchi, F. Capone, J. Colle, and J. Hiernaut, "Volatile Molecule PuO_3 Observed from Subliming Plutonium Dioxide," *Journal of Nuclear Materials*, **280**, 111, 2000.

J. Haschke and T. Ricketts, "Adsorption of Water on Plutonium Dioxide," *Journal of Alloys and Compounds*, **252**, 148, 1997.

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Further reading

J. Haschke and T. Allen, *Interactions of Plutonium Dioxide and Water and Oxygen-Hydrogen Mixtures*, LA-13537-MS, January 1999.

J.M. Haschke, T.H. Allen, and L.A. Morales, "Reaction of Plutonium Dioxide with Water: Formation and Properties of PuO_{2+x}." *Science*, 287, 2000.

with the plutonium oxide. Mass spectrometric analysis of gas samples taken after termination of the tests show that only water (H₂O) and hydrogen (H₂) were present in the gas phase. Qualitative results were similar to those observed at 298 K and suggest the following reaction:



This equation implies that a fraction of the plutonium is oxidized to an oxidation state greater than plutonium(IV) with a simultaneous increase in mass. Rate data for the reaction of plutonium dioxide and water versus temperature are shown in the figure below. This type of analysis, termed an Arrhenius plot, provides a measure of how difficult (or easy) the reaction proceeds as a function of temperature. The rate of reaction at 298 K is a value obtained from three independent kinetic measurements for the plutonium dioxide-plus-water reaction. The kinetic results from the microbalance and PVT measurements can be

described by a single relationship describing the dependence of the rate on temperature:

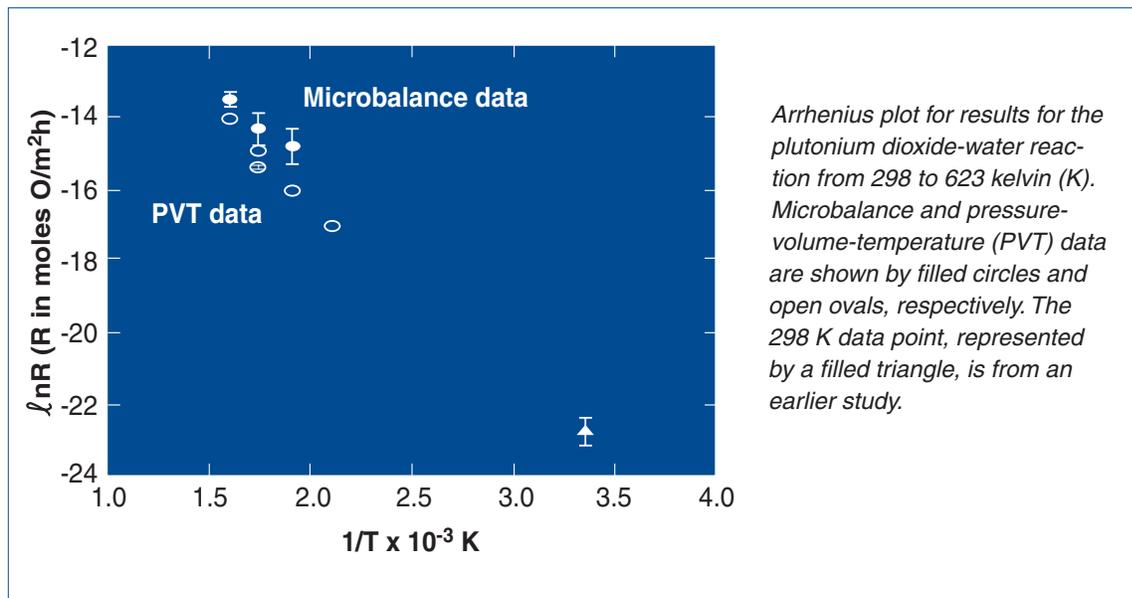
$$\ln[\text{Rate of reaction}] = -6.441 - (4706/T) \quad (2)$$

The activation energy (E_{act}; a quantitative indication of how hard it is to drive a reaction) for reaction 1 is 39.3 ± 2.5 kJ M⁻¹. The uncertainty in E_{act} results primarily from the uncertainty in the average rate at 298 K.

X-ray and neutron diffraction data show that the oxide product formed during reaction has a fluorite-related fcc structure derived from that of the dioxide. The results of eight measurements with calculated oxygen:plutonium ratios from 2.016 to 2.169 are shown in the figure on the next page. The lattice parameter of PuO_{2+x} is a linear function of composition:

$$a_o (\text{\AA}) = 5.3643 + 0.01764 \text{ O:Pu} \quad (3)$$

When the PuO_{2+x} product was heated above 673 K in subsequent thermogravimetric analysis (TGA) experiments, a mass loss was

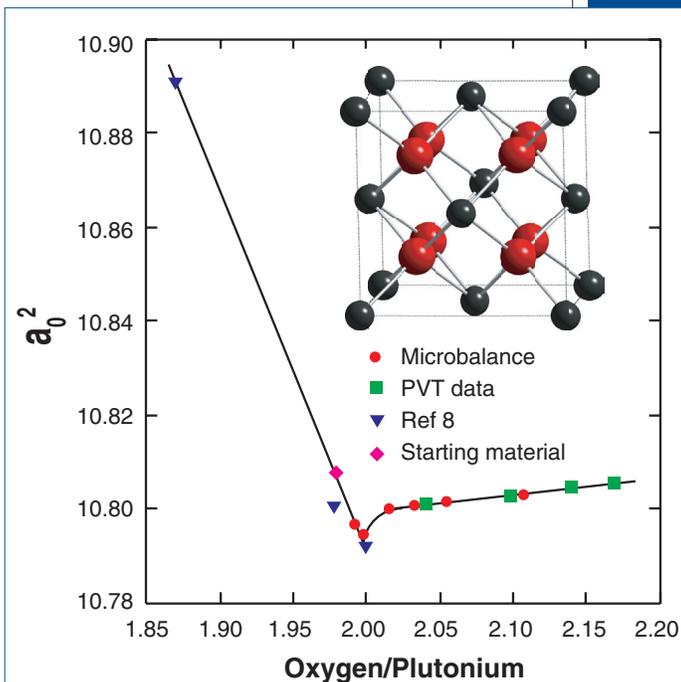


observed at approximately 633 K and the lattice constant of the resulting oxide returns to that of PuO_2 , indicating that PuO_{2+x} is stable only up to 633 K. The oxygen:plutonium ratio calculated from the measured mass loss in the TGA experiments and the hydrogen generation from the PVT experiments are in excellent agreement.

Kinetic results for oxidation of plutonium dioxide by water show that the reaction has a prominent temperature dependence from 298 to 623 K. The temperature dependence observed for the rate demonstrates that one is observing a chemical reaction with water, and not the result of radiolysis of water. The rate of a purely radiolytic process is expected to be independent of temperature at a fixed water pressure. If formation of PuO_{2+x} is promoted by radiolysis of water, the largest fractional contribution to the oxidation rate is anticipated at low temperature in a system with a high surface concentration of water.

Equation 3 describes the continuous variation of lattice parameter (a_0) with stoichiometry. This behavior nominally follows Vegard's Law (see sidebar on Page 8) and clearly indicates that O in the PuO_{2+x} structure exists as a solid-solution, not a new phase as previously conjectured. This slight lattice expansion, measured for the first time, suggests that additional oxygen is accommodated on interstitial sites in the fluorite lattice of plutonium dioxide. Whereas oxidation of plutonium(IV) on cationic sites of dioxide would tend to shrink the lattice, accommodation of oxide ions in interstitial lattice sites causes lattice expansion. The opposing changes are apparently of comparable magnitude, and the net effect is a small dependence of a_0 on the composition of PuO_{2+x} . These findings were published by J. Haschke, T. Allen, and L. Morales in 2000.

Additional studies using x-ray absorption near-edge structure (XANES) and x-ray



Dependence of the cubic lattice parameter, a_0 , on oxide composition of PuO_{2+x} . Oxygen/plutonium data for PuO_{2+x} from E. Gardner and others are shown by triangles. The composition of the starting oxide is given by the diamond. Values of a_0 obtained from the microbalance and pressure-volume-temperature (PVT) experiments are given by circles and squares, respectively. In the molecular structure inset, oxygen atoms are shown in red, and plutonium in black.

absorption fine structure (XAFS) were performed on PuO_{2+x} samples in which x was carefully varied by monitoring the amount of hydrogen gas produced in reaction 1. The position of the XANES edge demonstrated that the oxidation state of the PuO_{2+x} studied was a mixture of (IV) and (V), not (VI), as previously thought. These results were key in understanding how the oxygen was incorporated into the crystal lattice and were of enormous pragmatic use in interpreting environmental migration scenarios from real-world samples at Rocky Flats and Hanford in Washington.

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Vegard's Law

Crystalline solid-solution alloys have unit cell dimensions that are frequently linear with concentration. This property is referred to as Vegard's Law and has been generally assumed to imply that atomic volumes of the constituent elements are independent of the concentration or stoichiometry in a solid solution. For this model of solid solutions, an average lattice constant is assumed to arise from the close packing of hard-sphere atoms. Given this assumption, the average lattice parameter (R_{av}) is predicted to have a linear dependence on concentration

$$R_{av} = C_A R_A + C_B R_B$$

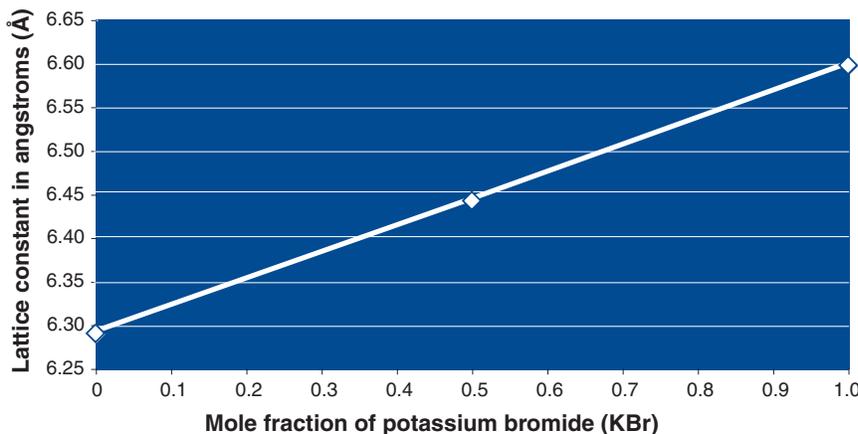
where R_A and R_B refer to the atomic radii of the pure elements A and B at concentration C_A and C_B , respectively.

A more complete description of the XAFS results and the local-range structure in PuO_{2+x} is provided on Page 16.

Taken together, the chemical, thermodynamic, crystallographic, and spectroscopic results form a self-consistent data set that provides a very strong case for the further oxidation of PuO₂ to a hyperstoichiometric solid solution denoted as PuO_{2+x} where the plutonium exists in a mixed-valence state.

Comparison of results for the plutonium-oxygen and uranium-oxygen systems suggests that the hyperstoichiometric regions above the dioxide compositions differ substantially. Although early work on the uranium system indicated the existence of a cubic UO_{2+x} solid solution at oxygen:uranium ratios up to 2.33, subsequent studies show that UO₂ coexists in equilibrium with the tetragonal U₄O₉ phase at temperatures below 573 K and that the UO_{2+x} phase is stable only at elevated temperatures. Cubic lattice parameters measured for the UO_{2+x} product suggest that a_0 decreases with increasing composition. Although UO_{2+x} and PuO_{2+x} apparently have similar structures with respect to the metal-atom lattice, it is evident that the manner in which oxygen—either as an oxide (O²⁻), a hydroxyl (OH), or water (H₂O)—is accommodated in the host lattice is notably different for UO_{2+x} and PuO_{2+x}. This difference prompts one to question the underlying reasons for this behavior and the potential impacts on our fundamental notions of electronic structure in the actinide oxides.

The stage is set for the next act in this unfolding adventure in actinide-materials science. Much work remains to be done to fully understand the relationships between the thermodynamic, crystallographic, and electronic properties of the actinide oxides. We are pursuing further studies with PuO_{2+x} and the alkali metal plutonates; however, the contrast between the uranium and plutonium oxides challenges our understanding of localized versus itinerant hybridization and the resulting consequences on crystal structure and physical properties. A systematic examination of all the actinide dioxides, with emphasis on uranium, neptunium, and plutonium (UO₂, NpO₂, and PuO₂) and their ability to accommodate extra lattice oxygen, is needed.



Lattice constant for the binary solid solution of potassium bromide (KBr) and potassium chloride (KCl).

An interpretation of the structure
of $\text{PuO}_{2.25}$ (Pu_4O_9) as $\text{Pu}_4\text{O}_8\text{OH}$

Proposing a hydroxide ion, rather than a central oxide ion, in the structure

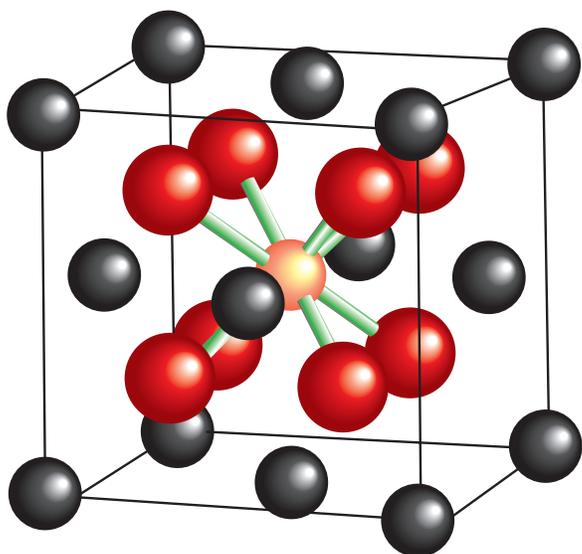
The preceding article described how, at temperatures of 50 to 350 degrees Celsius, the reaction of plutonium dioxide (PuO_2) with water yielded hydrogen gas and increased oxygen content in the solid. The composition of the resulting fluorite-related solid phase was described as PuO_{2+x} with $x=0.265$ as the oxygen increase limit. The importance of this finding is that plutonium dioxide is suggested to oxidize above a plutonium valence state of (IV) with a commensurate weight gain in the solid material. This finding is profound in that all other attempts to produce a binary oxide of plutonium with a higher valence have failed. That the material can be prepared in a nominal oxidation state higher than plutonium(IV) using water as an oxidant is especially puzzling. (Later articles will discuss the crucial role of water.)

A structure that purportedly contains all the salient features of the PuO_{2+x} entity is the unit cell description of PuO_2 with an added oxygen ion in the center of the structure. This structure, proposed in a report, "First-Principles Calculations of PuO_{2+x} ," that appeared in *Science*, Vol. 301, July 25, 2003, and described in the previous article, is drawn with strictly oxygen ions, yielding a unit cell composition of Pu_4O_9 . We propose replacing the central oxide in Pu_4O_9 with hydroxide, yielding $\text{Pu}_4\text{O}_8\text{OH}$.

There are several ways to achieve charge balance over the unit cell. One obvious way is to assign one plutonium atom a valence state of (VI). Alternatively, one could spread the charge over two plutonium core atoms in the unit cell and arrive at $\text{Pu}_2^{5+}\text{Pu}_2^{4+}\text{O}_9$, or possibly spread the charge over the entire unit cell core so that each plutonium atom that shares the charge is balanced equally with an average plutonium valence of +4.5. Experimental

data using x-ray absorption near edge structure (XANES) and x-ray photoelectron spectroscopy (XPS) unequivocally demonstrate that the PuO_{2+x} entity has plutonium(V) in the structure. (This will be explained in depth in the following articles.)

This new material, possessing plutonium with an overall valence greater than (IV)— PuO_{2+x} —has unit cell dimensions scarcely increased over those of PuO_2 —5.404 angstroms (Å) versus 5.3975 Å—in spite of the suggested placement of the extra oxide ion at body center, enclosed by the close-fitting subcell of eight oxide ions. The dominant x-ray



The molecular structure of plutonium dioxide (PuO_2) with an added oxygen ion (yellow) in the center. Oxygen atoms are shown in red, and plutonium in black.

This article was contributed by Robert Penneman (retired) and Mark Paffett of the Chemistry Division.

PROPOSING A HYDROXIDE ION

scattering arises from plutonium, indicating that the plutonium lattice positions remain essentially unchanged.

Structural determinations, whether performed using x-ray or neutron diffraction, have provided the preponderance of physical data upon which we base our understanding of structure and bonding in the actinide oxides and related compounds. More than half of all reported plutonium structures containing oxygen were determined by William H. Zachariasen before 1954 (see sidebar on Page 14). Coupled with single-crystal data obtained on the 5*f* fluoride compounds where structural data were available, Zachariasen summarized bond length-bond strength relationships among this class of materials and demonstrated the utility of this approach in predicting bond lengths when bond strengths are known or determining bond strengths when bond lengths are known.

Zachariasen bond length-bond strength formulations

Development of an adequate description of bond strengths and lengths has a long history, going back to 1929 and Linus Pauling's definition of bond strength as ion valence divided by its coordination number and Zachariasen's later derivation of the dependence of bond lengths on coordination number. By the middle of the twentieth century it was recognized that interpreting experimental bond lengths in terms of fixed radii (either ionic or covalent) was problematical and resulted in difficulty in explaining the large variation in bond lengths observed in the first coordination sphere of many crystalline solids that included the oxides and halides.

Based on data from well-established oxygen and halogen compounds of the 3*d*, 4*d*, 4*d*-5*f*, and 6*d*-5*f* elements, equations were formulated relating bond strengths to observed bond lengths.

These equations largely supplanted the use of ionic radii sums, which did not account for the observed variation in bond lengths. Although seldom referenced in recent literature, Zachariasen's summary equations provide a useful starting point for interpreting both oxygen and halogen compounds of the *d* and *f* elements.

In the Zachariasen model, bond strength is defined such that $s_{ij} = s_{ji}$ and relates to the bond between the *i*th and *j*th atoms in a structure

$$\sum_j s_{ij} = v_i \quad \text{and} \quad \sum_i s_{ji} = v_j,$$

where v_i and v_j are the valences and oxidation states of the two atoms. The length of the bond *D* between the two atoms is thus a function only of the strength of the bond. The great value of Zachariasen's work in this area was that it encompassed in a simple, quantitative equation the common observation that longer bonds are weaker than shorter bonds. The constants in the equation are based on x-ray structural measurements of bond distances in known structures, many provided by Zachariasen.

The goal is to find an empirical function that adequately describes and predicts bond lengths when bond strengths are known or that determines bond strengths when bond lengths are known. The power of this approach is that a preponderance of the actinide compounds containing oxygen can be shown to exhibit very predictable bond lengths. By using data from plutonium(IV)-oxygen, plutonium(V)-oxygen, and plutonium(VI)-oxygen distances (determined from many crystal structures), Zachariasen was able to derive the empirical logarithmic equation relating bond strength and bond lengths: $D(s) = D_1 - B \ln(s)$; where $D(s)$ is the bond length at bond strength (*s*), D_1 is the bond length at unit bond strength $s = 1$, and *B* is a scale factor.

“-Bln(s)” is the correction factor. It represents the deviation from single bond length, i.e., one of unit bond strength. This logarithmic correction shortens the bond length at bond strengths greater than unity (e.g., double bonds) and increases bond lengths for bond strengths less than a single bond.

For plutonium-oxygen bonds, D_1 values for plutonium(III), (IV), (V), and (VI) are 2.142, 2.094, 2.08, and 2.06 Å, respectively. For plutonium-oxygen bond strengths of unity or less, $B = 0.35$ is constant. However, the multiplier “B” increases as $0.35 + 0.12(s - 1)$ for bond strengths greater than unity, notably in structures containing the actinide(V) and (VI) dioxo cations, MO_2^+ and MO_2^{2+} . The function is linear over the range of $s = 1-2$ and displays curvature at s values below unity.

For plutonium(III)-fluorine bonds, the values for B and D_1 are 0.40 and 1.992, respectively. These values are necessary for the plutonium oxyfluoride (PuOF) structural example described below.

For plutonium and oxygen constituents of a structure, the sum of bond strengths to their neighbors is equal to their respective valences, usually to within 5 percent. In his last paper, published in 1980, Zachariasen concluded, “The remarkable fact is that the equation: $D(s) = D_1 - B \ln(s)$, normally predicts the bond length to 0.02 Å when s is known.”

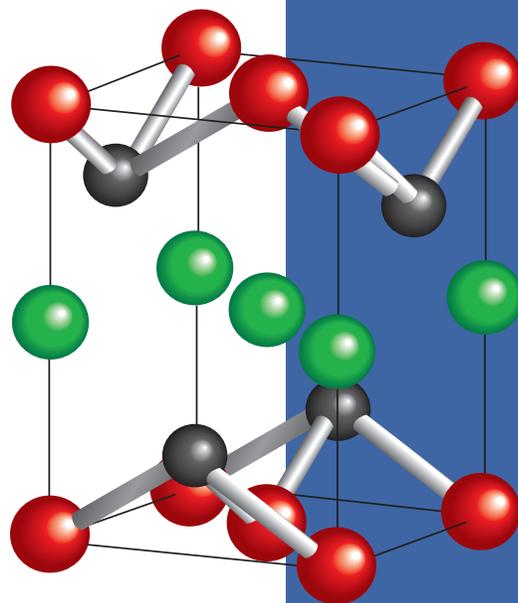
Applying Zachariasen’s formulas to simple compounds

By applying Zachariasen’s formulas to a number of relatively simple plutonium compounds, we arrive at a more complete and correct interpretation for the bond lengths and connections with valence in specific solid compounds. We begin by discussing the relatively simple compound PuOF and then use similar logic to examine the putative Pu_4O_9 (“ $\text{PuO}_{2.25}$ ”) structure, which has also been described as the hyperstoichiometric PuO_{2+x} entity.

An example of the utility of Zachariasen’s approach is found in its ability to predict the correct bond lengths of oxygen and fluorine in PuOF. In this example, the location of the light atoms, oxygen and fluorine, were erroneously determined when ionic radii were used to assign their respective positions in trivalent PuOF, a compound in which each plutonium atom is coordinated by two sets of four anions at 2.569 Å and 2.385 Å. Since the ionic radius of the oxide (O^{2-}) is greater than that of the fluoride (F^{-1}), the longer distance was originally assigned to plutonium-oxygen.

Zachariasen later interchanged the oxide and fluoride positions based on three arguments. First, the (-2) oxide charge shared by four atoms of plutonium(III) yields plutonium-oxygen bond strengths, $s = 0.5$, and dictates assignment of the shorter bond distance to oxygen. Second, the (-1) fluoride charge shared equally by four atoms of plutonium(III) yields plutonium-fluorine bond strengths, $s = 0.25$, and thus the longer plutonium-fluorine bond distance. Third, comparison of the bond strength sums makes the interchange clearly preferable.

Original selection: Pu-4O, 2.569 Å; $s = 0.2952$;
Pu-4F, 2.385 Å; $s = 0.3745$
Old bond strength sum: Pu = 2.68; O = 1.18;
F = 1.50



William H. Zachariasen's correct interpretation of the crystal structure for plutonium oxyfluoride (PuOF). Fluorine atoms are shown in green, oxygen in red, and plutonium in black.

PROPOSING A HYDROXIDE ION

Preferred interchanged positions: Pu-4O, 2.385 Å, $s = 0.4997$; Pu-4F = 2.569 Å, $s = 0.2363$
New bond strength sum: Pu = 2.94; O = 2.00; F = 0.95

The sum of the bond strengths over the elements is noted to be much more consistent with chemical intuition. This example demonstrates the simplicity and utility of the Zachariasen bond strength-bond length relationship and its use in discriminating between plausible ligated species. The plutonium oxyfluoride example is particularly germane because of the crystal chemical similarities between the fluorine and hydroxyl ligands.

It is customary to formally denote the actinide MO_2^+ and MO_2^{2+} cations as double-bonded. At bond strength $s = 2$, the plutonium(V)-oxygen bond distance is 1.85 Å and the plutonium(VI)-oxygen bond distance is 1.73 Å. Bond distances this short are only observed in discrete molecules and rarely occur in solids. Usually, bonding to other ions in the structure reduces the metal-oxygen bond strength and lengthens the multiple bond, providing a range of longer distances. We retain the double bond formality but recognize that its strength is more often less than 2.

Applying Zachariasen's formulas to Pu_4O_9 ("PuO_{2.25}") and the body-centered oxide ion

Zachariasen's bond strength-bond length relationships are applied to the Pu_4O_9 ($\text{PuO}_{2.25}$) entity. The value for the cell edge of cubic PuO_{2+x} of highest oxygen content is 5.404 Å, yielding a body diagonal of 9.36 Å. The added oxygen is placed at the body center, midway along the body diagonal at 4.68 Å. The plutonium(IV)-oxygen distance along this diagonal is 2.33 Å at $s = 0.5$ (as shown in the figure on Page 9 with the central yellow sphere). However, increasing the valence of one of the plutonium atoms to (V) yields

$s = 1.5$ and the smaller value of 1.91 Å for the plutonium(V)-oxygen bond distance. Allowing 2×1.4 Å for the Van Der Waal (VDW) radii sum of the two oxygens and adding the plutonium(V)-oxygen distance of 1.9 Å yields $2.8 + 1.9 = 4.7$ Å, which agrees well with the experimental value of 4.68 Å for half the body diagonal.

Conversion of a corner plutonium(IV) to (V) has an effect: increasing $s = 0.5$ to $s = 1.5$ for the plutonium(V)-oxygen bond on the diagonal leaves unchanged its seven other plutonium-oxygen bonds at $s = 0.5$ for a bond sum of $3.5 + 1.5 = 5$. This has the strong implication that the cell dimensions will show little size change from those of plutonium dioxide itself, consistent with the x-ray diffraction results described in Luis Morales' article on Page 3.

Withdrawal of the oxygen 0.42 Å along the body diagonal from its tetrahedral site lengthens somewhat the plutonium(IV)-oxygen bonds on the threefold axis. This may account for the direction and magnitude of the +0.007 Å change in cell dimensions (5.3975 to 5.404 Å). Oxygen volume assignment in compounds containing plutonium(V) is 18 \AA^3 and is applicable for oxide, hydroxyl, and water. Using 18 \AA^3 for the nine oxygen atoms per unit cell provides a cell volume for Pu_4O_9 of 162 \AA^3 versus 158 \AA^3 observed.

However, a surprising result arises with the bond strength sum around the central oxide. Octahedral coordination at the body center by the six face-centered plutonium(IV) ions occurs at distances of half the cell edge, or 2.702 Å. This plutonium-oxygen bond distance corresponds to $s = 0.176$ and an oxygen valence sum of 1.06, compared to a plutonium(IV)-oxygen distance of 2.72 Å calculated for $s = 1/6$. (Note: the bond strength sum normally agrees to within 0.1 valence units and the bond length to 0.02 \AA when s is known.)

This unit charge further substantiates a central ion and the strong possibility of a

central hydroxyl ion instead of an oxide ion. A central oxide ion requires $s = 2/6$ and a much shorter bond distance of 2.48 Å (not observed). An oxide ion centered in the cubic array of eight oxygen ions would likely expand the lattice by repulsion. Hydrogen bonding by the hydroxyl ion, as well as its lower charge, would attenuate repulsion.

J. Haschke and others, in their article "Reaction of Plutonium Dioxide with Water: Formation and Properties of PuO_{2+x} " which appeared in *Science*, Vol. 287, Jan. 14, 2000, reported $\text{PuO}_{2.265}$ as the excess "oxide" content of the solid without discussing that it exceeded the $O = 2.25$ limit imposed by Pu_4O_9 . This further supports our proposal for $\text{Pu}_4\text{O}_8\text{OH}$, with the value of 0.265 for the "oxygen" excess over PuO_2 obtained directly as a result of substituting hydroxyl for an oxygen in Pu_4O_9 (that is $17/16 \times 0.25 = 0.2656$).

Although a central hydroxyl ion can account for the bulk of the increased oxygen uptake, additional detail is needed to account for the spectroscopic observations described in subsequent articles. In the next article, reduced extended x-ray absorption fine structure (EXAFS) spectroscopy data for PuO_{2+x} highlight the impact of superstructure (structure over multiple-unit cells) and loss of order over multiple-unit cells.

These results, taken with our understanding of how extra lattice oxygen incorporates into the uranium oxide, UO_2 , as the UO_{2+x} entity, provide the framework for describing the complex structural manifestations of the water-corrosion reaction.

Conclusions

The short range, local order (structure) of the Pu_4O_9 entity is better described as $\text{Pu}_4\text{O}_8\text{OH}$. Bond strength-bond length arguments justify the location of a hydroxide ion, rather than a central oxide ion, in a plutonium dioxide structure, providing an alternative interpretation for the

experimental data on plutonium dioxide oxidation by water. A central oxide is rejected on the basis of its bond sum. A central oxide requires $\text{PuO}_{2.25}$ while substitution of hydroxyl for oxide accounts precisely for the experimental value of "excess" oxygen in $\text{PuO}_{2.265}$ yielding $\text{PuO}_2(\text{OH})_{0.249}$.

Increasing the valence to plutonium(VI) is similarly rejected on the basis of the sum about the plutonium(VI)-oxygen component. The bond strength sum around the plutonium(V)-oxygen component is normal and supports minimal cell dimension change. However, plutonium(VI)-oxygen at $s = 2.0$ requires that the seven remaining plutonium(IV)-oxygen bonds increase from $s = 0.5$ to 0.571, that is $(7 \times 0.571 + 2.0 = 6)$, resulting in cell dimensions not present for a plutonium(VI)-oxygen component.

Zachariasen's bond strength-bond length relationships are based on a multitude of actinide structures that support this contention. This approach has found utility for simple structural bond length and bond strength determinations but is limited in structures that display larger deviations, possibly resulting from superstructure disorder.

It has been firmly established that PuO_2 reacts with water at intermediate temperatures, yielding hydrogen gas simultaneously with an increase in the oxygen content of the solid, for which researchers suggested a central oxide ion in Pu_4O_9 . The essence of our current work is that a central hydroxyl fits the data better, yielding the formula $\text{Pu}_4\text{O}_8\text{OH}$, containing one plutonium(V).

This view of the structure with a hydroxide will be shown to be more consistent with XPS and EXAFS data and will be discussed in the following articles. However, the spectroscopic observations call for more work to be done to unequivocally determine the wealth of structural changes manifested when plutonium dioxide is corroded by water.

Zachariasen led the way Sixty years of structural determinations of the 5f elements ... or, why are the actinides so named?

Sixty years ago a surprisingly succinct memo summarized our knowledge of the structure of the actinide oxides. The memo is historically significant because the author, William H. Zachariasen, wrote that based on x-ray structural determinations of thorium, uranium, and plutonium compounds, fairly conclusive proof of the filling of the 5f shell had been obtained.

Zachariasen, having examined the x-ray pattern of a sample of neptunium oxide (NpO₂) wrote in part:

The interpretation of the diffraction pattern and crystal-chemical considerations permit me to make the following statements, all of which can be regarded as quite certain: The submitted sample is NpO₂ ... The radius of Np⁺⁴ is thus 0.015 Å larger than that of Pu⁺⁴, 0.016 Å smaller than that of U⁺⁴, and nearly identical with that of Ce⁺⁴.

I believe that a new set of 'rare earth' elements has made its appearance. I believe that the persistent valence is four, so that thorium is to be regarded as the prototype; just a lanthanum is the prototype of the regular rare earth elements.

This memo predated Glenn Seaborg's own "Actinide Hypothesis" memo of July 14, 1944. The table Zachariasen included in his memo for the results of NpO₂ compared with those obtained earlier for isomorphous dioxides, coming at such an early time in the Manhattan Project, was quite sensational and also controversial. The controversy stems from the how the new series should be most appropriately labeled and viewed.

Ultimately, Seaborg's view prevailed because of the 5f electron configuration of curium and the stability of the lower-valent states at the series end. Despite this outcome, Zachariasen maintained his

position over the years that the "name actinide is not acceptable because thorium is never actinium-like." He thereafter called the new series the 5f elements and pointed out that not until elements 95 and 96 (americium and curium) were the elements rare-earth-like, and

William H. Zachariasen and his 1944 memo.

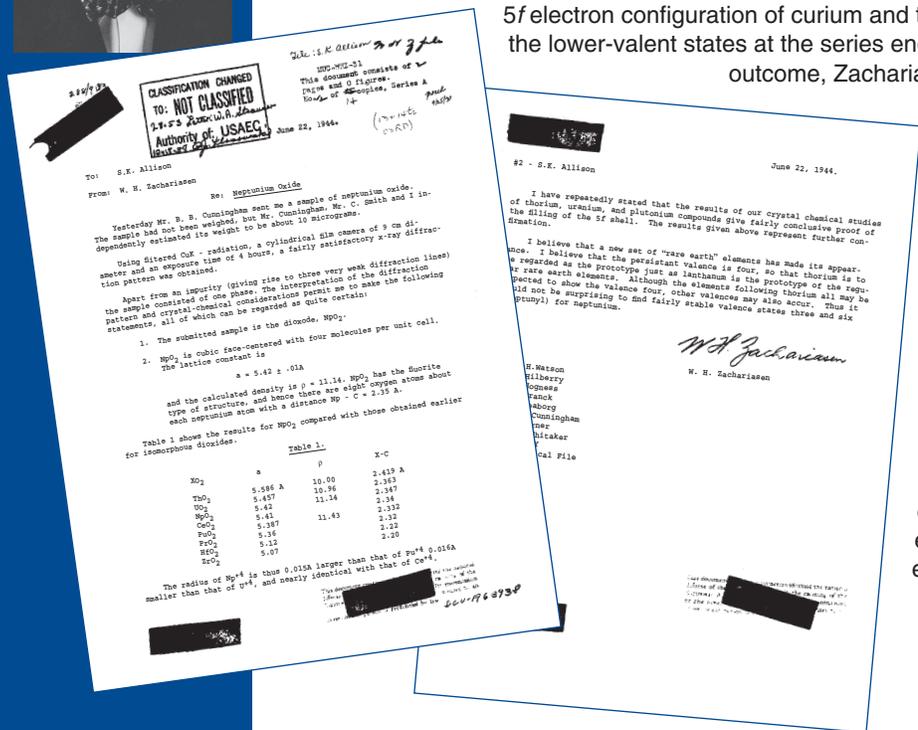
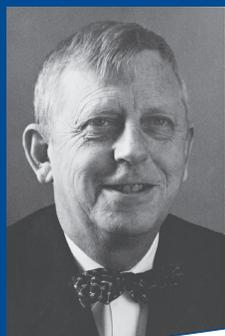


Table 1 shows the results for NpO₂ compared with those obtained earlier for isomorphous dioxides.

	a	b	c	Z-C
ThO ₂	5.286 Å	10.00	2.418 Å	2.953
UO ₂	5.457	10.96	2.367	2.94
NpO ₂	5.42	11.16	2.34	2.93
PuO ₂	5.41	11.43	2.33	2.92
CeO ₂	5.387		2.22	2.92
PrO ₂	5.36		2.20	
LaO ₂	5.27		2.20	

further, that the metal dioxide structure (MO_2) persisted from thorium dioxide (ThO_2) to californium dioxide (CfO_2), or elements 90 through 98.

Zachariasen was a giant among early Manhattan Project scientists and was notable for many firsts. He was a world figure in x-ray structural analysis and published more than 200 papers, the first when he was just 19. The significance of his accomplishments and background is captured in the inaugural issue of *Los Alamos Science*, published in the summer of 1980.

In early 1942, the fledgling Metallurgical Laboratory (plutonium) project was established at the University of Chicago—away from the East and West Coasts where the work had originated—in case of attack. In late 1943, Arthur Compton, Nobel laureate and head of the physics department at Chicago, asked Zachariasen to help explain the chemistry of the new element, plutonium, then available only in microgram-scale preparations. Zachariasen's impact was immediate, demonstrating, "that satisfactory x-ray patterns of plutonium preparations on the 10-microgram scale often could provide positive identification of the phase or phases present...."

Summarizing his three years working on compounds produced by Seaborg's group, Zachariasen wrote:

For the past three years within the plutonium project, I carried out partial or complete crystal structure determinations of 140 different compounds of plutonium, neptunium, uranium, thorium or rare earth elements. My collaborator Dr. Rose Mooney made similar determinations of an additional 20 compounds.

All but three of the first 25 plutonium compounds to be identified were identified by the x-ray diffraction method. Every one of the compounds of actinium, protactinium, neptunium and americium whose existence is now established was identified by the x-ray diffraction method, and solely by that method.

In fact, even today among structural determinations of actinide oxides, Zachariasen's scientific output comprises more than half of the reported structures.

In the 1950s, Zachariasen came to Los Alamos in the summer to work out the complicated structures of plutonium metal. Of that work, A.S. Coffinberry and W.N. Miner wrote in their book, *The Metal Plutonium*: "It is highly improbable that any scientist other than Zachariasen could have solved the three structures as complex as those of alpha, beta and gamma plutonium from powder patterns alone."

Powerful tool for probing molecules
**X-ray absorption fine structure spectroscopy
 determines local structure and bonding
 in actinide-oxide structural variants**

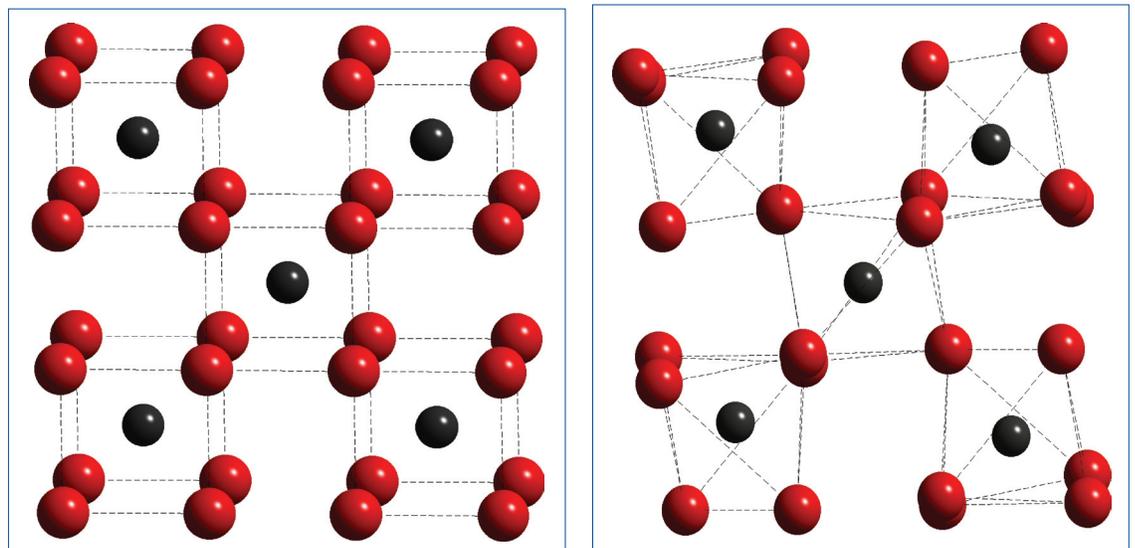
This article was
 contributed by
 Steven Conradson
 of the Materials
 Science and
 Technology Division.

Actinide oxides (AnO_2) have crystalline structures that are relatively open. They are potentially “reactive” because the openness of their structures makes them easily invaded by or reactive toward other atoms. Actinide oxides are of great scientific interest because understanding how oxygen atoms are added and removed in actinide-oxide solids is essential for predicting their behavior. For example, some scientists believe that the presence of small amounts of plutonium(VI) in nonstoichiometric plutonium dioxide (PuO_{2+x}) may increase the solubility of this environmentally hazardous compound. Likewise, corrosion and other chemical reactions are affected by changes in molecular structure of these solids.

Data obtained through x-ray diffraction show that actinide oxides of general composition AnO_{2-x} form a cubic fluorite-type phase over the composition range of $AnO_{1.6}$ to $AnO_{2.0}$ for thorium through californium, as illustrated in the figures below. The stoichiometric $AnO_{2.0}$ lattice consists of a face-centered cubic (fcc) arrangement of metal atoms in six-fold “octahedral” lattice sites. Each metal atom is surrounded by eight oxygen atoms at the corners of a cube, and each adjacent cube has a vacant metal site. The intermediate phase compositions and structures displaying oxygen:metal ratios between 1.6 and 2.0 are realized by omission of oxygen atoms in a regular way. Except for small shifts away from the vacant oxygen sites, the metal atoms always maintain their fcc positions.

Some actinide-oxide solids can be further oxidized, as in the case of uranium or plutonium dioxide, with the simultaneous addition of oxygen atoms to the lattice. For the composition range AnO_{2+x} where x falls

Actinide oxides have relatively open crystalline structures that make them easily invaded by other atoms. The actinide-oxide (AnO_2) lattice structure on the left exhibits a fluorite crystalline structure with alternating empty and occupied oxygen cubes. The lattice structure on the right shows how Pu_2O_3 is produced from plutonium dioxide (PuO_2) by removing every fourth oxygen atom from the lattice.



between 0 and 0.25, x-ray diffraction analyses reveal a single fcc phase with a fluorite-related structure and a slightly expanded lattice, consistent with the formation of a solid-solution for AnO_{2+x} . Many actinide-oxide-type materials also react with water that can lead to substitution of the O^{2-} ion with a hydroxide ion (OH^-) or water molecule (H_2O), leading to a more complex overall description of coordination where y and z are stoichiometry descriptors that account for this net coordination of OH^- and H_2O , respectively ($\text{AnO}_{2+x-y}(\text{OH})_{2y} \cdot z\text{H}_2\text{O}$ for example).

One of the more remarkable aspects of the class of solids AnO_{2+x} is the ability to add or remove oxygen atoms with simultaneous oxidation or reduction of the actinide ions while conserving the basic crystallographic structure. In many cases the addition or removal of oxygen (O) atoms results in diffraction patterns from the cubic actinide sublattice that translate into changes of only a few hundredths of an angstrom (\AA) in lattice constant. This conservation of the structure indicates the formation of structurally similar phases in which the oxygen atoms occupy interstitial lattice sites that retain most of the functional features of the original unit cell.

For example, cubic Pu_2O_3 is produced from PuO_2 by the sequential removal of every fourth oxygen atom from the lattice, as shown in the right-hand figure on the previous page. Similarly, sixteen distinct phases have been identified as the oxygen content in uranium oxide compounds increases between UO_2 and UO_3 . These structures transform into each other by small expansions and contractions of the uranium sublattice, apparently induced by different, ordered arrangements of the oxygen atoms as more are added to the original uranium dioxide structure. The extra oxygen atoms or vacancies within the crystal form clusters within the host crystal because of the stability of these putative phases relative to a random distribution of oxygen atoms.

Based on interpretations of both x-ray and neutron diffraction data following addition or loss of oxygen atoms, highly detailed mechanisms of phase and structure formation have been described for the uranium dioxide UO_{2+x} system. The salient attribute of these mechanisms is that extra lattice oxygen atoms are added through displacements and rearrangements within the oxygen sublattice, using the empty space of the unoccupied cubic sites. The additional charge on the uranium ion tends to be dispersed rather than localized and is accommodated by small (less than 0.15 \AA) reductions in some uranium-oxygen bond lengths (balanced by expansions of others) and increases the number of nearest neighbors bonded to the uranium atoms in the lattice (i.e., the coordination number). There are, however, problems with these models.

Conceptually, this delocalized charge distribution is inconsistent with the known molecular coordination chemistry of the lighter actinides. In molecular complexes of higher-valent light actinides, discrete oxo groups are found at very short (less than 1.85 \AA) actinide-oxygen distances as well as at lower total coordination numbers. The higher actinide charge is thus stabilized by fewer oxygen near-neighbors but some shorter, much more covalent bonds.

It is difficult to determine the correct structures of the disordered, mixed-valent AnO_{2+x} solids by conventional crystallographic analysis from diffraction data alone, typically because a range of structural solutions is possible. In highly ordered materials, atoms in a crystalline lattice exhibit very regular repeat units; this is called long-range order and is typically studied using x-ray or neutron diffraction techniques. To directly probe chemical speciation and local structure that will include aperiodic components in $\text{AnO}_{2+x-y}(\text{OH})_{2y} \cdot z\text{H}_2\text{O}$ solids independent of their long-range order, we have made extensive use of extended x-ray

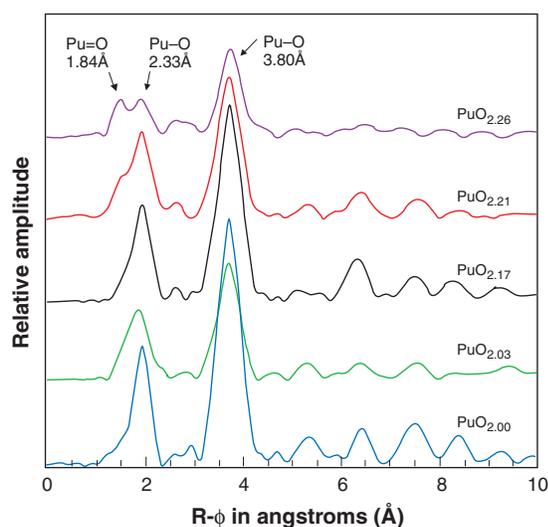
X-RAY
ABSORPTION

Extended x-ray absorption fine structure (EXAFS) data shows the splitting of the first oxygen shell (indicated by the double peaks) in the $\text{PuO}_{2.26}$ spectrum (purple). The spectra also show that the relative amplitude of the peaks decreases as x increases from $\text{PuO}_{2.00}$ to $\text{PuO}_{2.26}$. The periodic oscillations also become more washed out as x increases, meaning the atoms become more disordered.

absorption fine structure (EXAFS) spectroscopy. This experiment is performed at Stanford Synchrotron Radiation Laboratory and can provide information about the metal oxidation state, bond distances, and types and numbers of atoms coordinated to the metal center. The application of this technique provides unique characterization and insight into local bonding in a number of PuO_{2+x} and UO_{2+x} solids where x varies from 0 to 0.25. (See ARQ 1st quarter 2004 for applications in actinide solution chemistry.)

For plutonium, we have investigated more than two dozen PuO_{2+x} compounds prepared by a variety of methods, including hydrolysis and precipitation of the aqueous plutonium(IV) ion, and by the heterogeneous oxidation of plutonium metal and oxide with water vapor, oxygen, or both. The first finding, based on a simple comparison of the spectra with the one calculated from the crystallographic structure, is that simple, highly ordered plutonium dioxide is rather rare and is not typically obtained simply by firing or calcining plutonium compounds in air at high temperatures.

Fourier transforms of EXAFS data for selected plutonium oxide compounds are shown in the figure below. (See Page 24 for



an explanation of XAFS data analysis.) For stoichiometric, ordered $\text{PuO}_{2.0}$ the first peak in the Fourier transform is the contribution of the eight nearest-neighbor oxygen atoms at 2.33 Å, well separated from the more distant second nearest-neighbor peak of twelve plutonium atoms at 3.80 Å (the peaks in the figure at left are all phase-shifted to lower R).

Regular features from the well-ordered extended structure subsequently continue out through very high distance from the central absorbing atom. This spectrum is consistent with the crystal structure shown on Page 16 on the left. An alternative drawing of the basic structure from the perspective of a central plutonium atom is shown at different internuclear distances on the next page to emphasize the different “shells” of atoms observed in an EXAFS experiment.

However, as x increases from $\text{PuO}_{2.00}$ to $\text{PuO}_{2.25}$ the amplitudes of all of the peaks in the Fourier transform decrease monotonically, indicative of diminished order via displacements of the plutonium and oxygen atoms from their lattice sites coupled to the incorporation of the nonstoichiometric oxygen atoms into interstitial, essentially defect, sites. What contradicts the current models in this process is the splitting of the first oxygen shell and the appearance of a short plutonium-oxygen bond distance of 1.84 Å.

Diffraction techniques that probe long-range order have never observed this phenomenon, but the bond distance is similar to those found in discrete plutonium-oxygen bonds in molecular compounds that range from 1.73 Å for plutonium(VI) compounds to 1.85 Å for plutonium(V) compounds. These results show that as the plutonium center becomes partially oxidized in PuO_{2+x} there is a strong driving force to form short, strong, covalent plutonium-oxygen bonds.

The addition of extra lattice oxygen into the solids produces a number of other

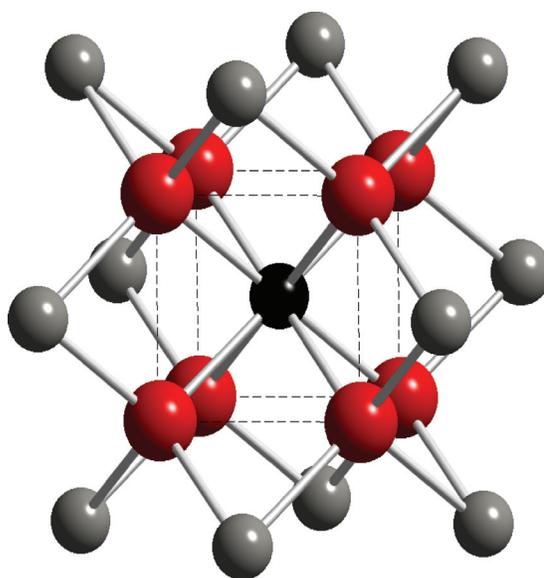
systematic changes in the spectra from the various plutonium oxide compounds. Disorder in the nearest-neighbor oxygen shell resulting from plutonium-oxygen bonding that can be assigned to hydroxyl and possibly water ligands is evident in some cases.

Furthermore, the directly coordinated oxygen near-neighbor shells are supplemented by longer plutonium-oxygen bond distances that result from the mirroring of these displacements on the neighboring plutonium atoms and show up as peaks between the crystallographic oxygen and plutonium shells at 1.8 and 3.8 Å, respectively (the peaks are phase shifted from their actual distances).

What is unexpected, however, is that these additional shells of oxygen atoms are often found in materials following thermal treatments (to 1,000 degrees Celsius) in an oxygen-containing environment. Following this calcination step, nominal plutonium dioxide solids are cooled in an ambient processing environment. Unless preventative steps are taken, such as cooling in an extremely dry ambient atmosphere with immediate packaging, the rates of water uptake, hydrolysis, and coordination to plutonium ions within the lattice are sufficient to generate measurable quantities of extra lattice oxygen as protonated ligands (ligands with added protons) that are not associated with oxidation.

In addition, the plutonium-hydroxide bonds remain stable to moderately high temperatures (typically 600 degrees Celsius; see the following article). Thus, plutonium dioxide displays a tenacious affinity for water-derived extra lattice oxygen constituents.

For PuO_{2+x} compounds processed at elevated temperature, the reduced XAFS data exhibit narrower features with much greater relative amplitudes for the nearest-neighbor oxygen peak, thus indicating a corresponding higher degree of local order in the plutonium-oxygen distributions in the compounds.



For the PuO_{2+x} spectra shown on the previous page, the near-neighbor, singly bound oxygen region with plutonium-oxygen bond distances between 2.15 and 2.45 Å always requires at least two scattering shell contributors for an adequate fit, with one above and one below 2.3 Å. The 0.10 to 0.18 Å separation between these two shells is right at the 0.11 Å data resolution limit. In addition, fits to some spectra are significantly improved by including a third oxygen shell to this region. In these cases, the short plutonium-oxygen bond distance decreases to less than 2.15 Å, one remains between 2.25 and 2.30 Å, and the longer one shifts above 2.30 Å.

These limitations demonstrate that EXAFS also suffers from the problem that more than one solution can be obtained for the overall distribution function described by multiple curve fits. The solution(s) does not necessarily fit to the precise values of the explicit parameters such as numbers of coordinating atoms, distances, and Debye-Waller factors (the Debye-Waller factor of a near-neighbor scatter

X-ray absorption fine structure (XAFS) spectroscopy provides information about the number of atoms and their interatomic distance from a central target atom. The crystalline structure of plutonium dioxide (PuO_2) shows cubic symmetry. There are eight near-neighbor oxygen atoms (shown in red) that all sit at 2.33 angstroms (Å) from the central plutonium atom (black). There are also 12 neighboring plutonium atoms (gray) at an interatomic distance of 3.81 Å from the central plutonium atom. It is this combination of the number of near-neighbor atoms, their elemental identities, and their interatomic distances that uniquely define the chemical structure using XAFS spectroscopy.

X-RAY
ABSORPTION

accounts for the mean-square fluctuations and thermal disorder). Nevertheless, general aspects of the XAFS curve-fit results indicate that the type of ligand largely determines bond lengths, as is typical of coordination chemistry of molecular complexes.

In fact, the plutonium-oxygen bond lengths determined by curve fits of the XAFS data are so similar to those found in molecular coordination compounds that they can be assigned to specific ligands based on these internuclear distances: coordinated hydroxyls for the plutonium-oxygen bond distance between 2.25 and 2.35 Å, coordinated oxide ions for the plutonium-oxygen bond distance between 2.35 and 2.40 Å, and coordinated water for the plutonium-oxygen bond distance beyond 2.45 Å. This scheme is not necessarily rigorous; the longer distance(s) could also reflect particular bridging ligand geometries where a coordinated oxygen entity in effect bridges two plutonium atoms with an elongation of bond length.

Although these results show the affinity of the plutonium in PuO_2 for water, the primary issue in PuO_{2+x} remains the disposition of the added oxygen associated with oxidation that increases the valence of the plutonium. The critical comparative sample is $\text{PuO}_{2.26}$. The first shell of oxygen near-neighbor atoms shows two clearly resolved peaks of relatively low but similar amplitude; the plutonium-oxygen nearest-neighbor distribution is obviously more complicated than the single oxygen shell of the highly ordered PuO_2 . The peak at lower R , whose large relative amplitude clearly suggests a prominent structural feature, occurs almost 0.6 Å below the oxygen peak obtained from the ordered PuO_2 samples.

Curve fits show that these two peaks require four shells to be completely fit. Despite the limitations of the curve-fitting process, three of these correspond to singly bound oxygen ligands, with overlapping plutonium-oxygen bond distances of 2.13, 2.28, and 2.41 Å,

giving a broad oxygen distribution. The fourth shell, completely resolved from the others and essential in fitting the lower peak in the Fourier transform, has a plutonium-oxygen bond distance of 1.84 Å. Bond lengths this short in both molecular complexes and extended solids are found only for the multiply bound oxo groups associated with valences of (V) and (VI) in MO_2^+ and MO_2^{2+} units.

Oxo groups can be defined as oxygen shells with actinide(V, VI, VII)-oxygen bond distances less than or equal to 1.9 Å that involve actinide-oxygen bonds of multiple-bond order, and that usually impose additional constraints on actinide coordination geometry in unit cell models. The presence of oxo groups in $\text{PuO}_{2.26}$ demonstrates that an oxygen shell near this distance should be included in the basic structural model that is the starting point for the curve fits for the spectra of all samples. A more detailed inspection of this region shows that there are trends, especially in the real component of the transform, by which the presence of an oxo shell can be directly inferred from the spectra without resort to curve fitting, further corroborating its presence.

The observation of an apparently stable, disordered, mixed-valence form of PuO_{2+x} without any indication of phase separation poses a conundrum in our understanding of this material. Recent independent electronic-structure calculations place the extra lattice oxygen in the interstitial site formed by the empty cube of oxygen atoms and without consideration of oxo group formation. These calculations are inconsistent with XAFS measurements; a 1.9-Å plutonium-oxygen bond distance places the oxygen within the oxygen cube already occupied by a plutonium ion.

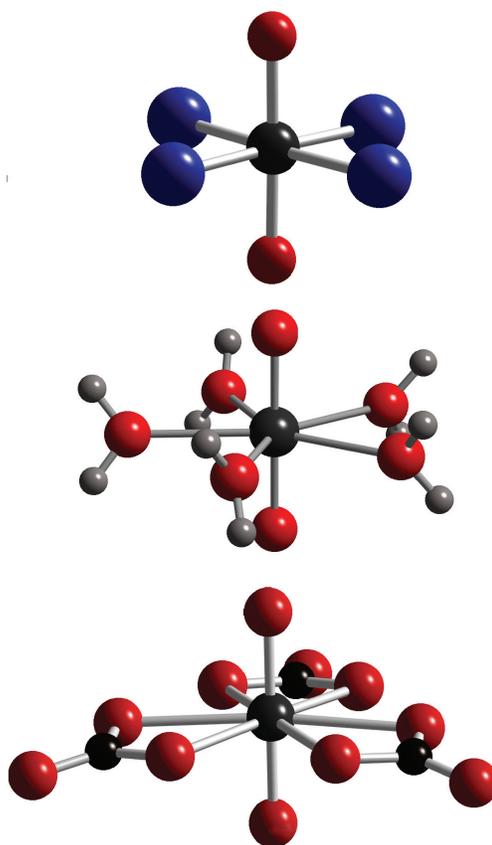
In solid crystals comprised of many unit cells, cooperative and collective effects that include entropic statistical effects can be important, such as the incorporation of extra

lattice oxygen into UO_{2+x} as $\text{UO}_{2.25}$ -type clusters. The microscopic structural attributes identified by EXAFS in the PuO_{2+x} series suggest that entropy in combination with different bonding types, the combination of which will only become significant in crystals containing many more atoms than can be included in the calculations, may be a significant contributing factor in their structural evolution. These structural attributes must, however, be inferred because XAFS data does not give direct information on nanoscale ordering.

Although there are exceptions, the most common structural motif for actinide ions in their higher oxidation states (V and VI) is the trans dioxo geometry, in which two oxygen atoms form strong covalent bonds with the actinide ion to form a linear actinyl unit, $\text{O}=\text{An}=\text{O}$. All other donor atoms form bonds to the molecule in an equatorial plane that is perpendicular to the linear $\text{O}=\text{An}=\text{O}$ unit. The equatorial plane can accommodate four, five, or six atoms. In the figure at left the local bonding about a central actinide AnO_2^{2+} ion is shown for $\text{PuO}_2\text{Cl}_4^{2-}$, $\text{PuO}_2(\text{H}_2\text{O})_5^{2+}$, and $\text{PuO}_2(\text{CO}_3)_3^{4-}$ as examples of four, five, and six coordination in the equatorial plane.

Scenarios can be devised for incorporating this PuO_2^+ local bonding geometry in the extended plutonium dioxide lattice. The easiest way is to place the extra lattice oxygen atoms midway between two plutonium ions, so that they reside on the midpoint of a [100] directional vector of a PuO_8 cube. This is indicated schematically in the figures on the next page. The top figure shows three adjacent cubes of oxygen atoms where the center cube is occupied by a central plutonium atom and the two adjacent cubes are vacant. In the second figure, extra oxygen atoms (blue) are added to these vacancies. The resulting Pu–O bond distance of 2.7 Å is clearly not consistent with the EXAFS data.

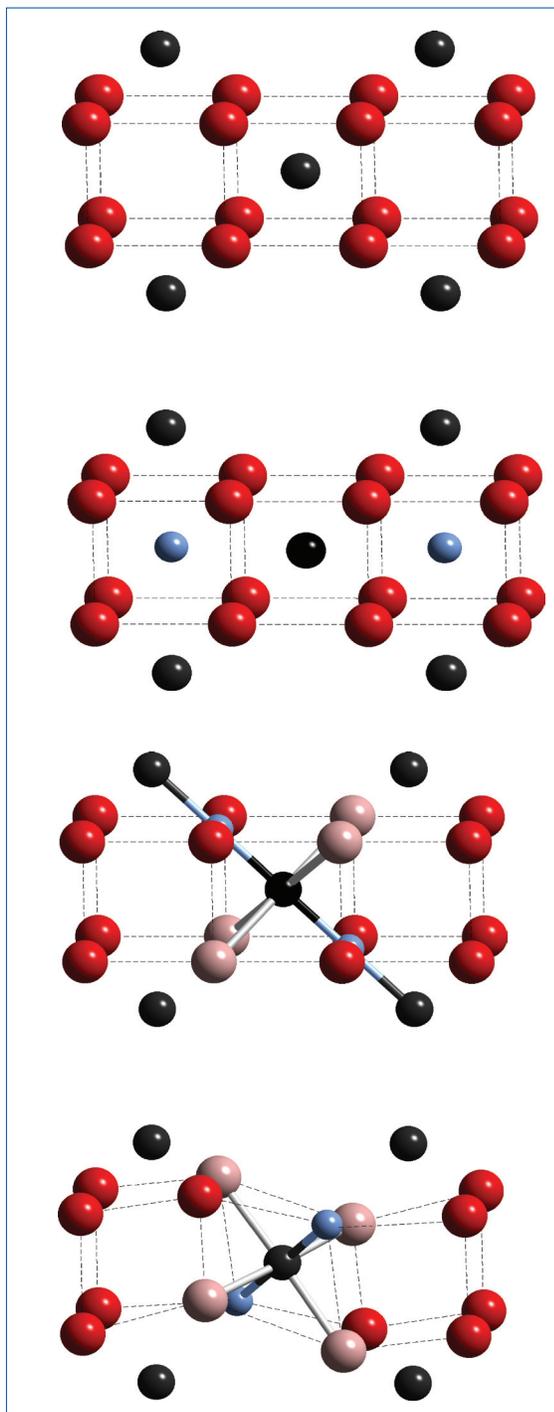
The third structure shows the addition of two oxo groups with Pu–O = 1.9 Å normal to



a [110] plane of the PuO_8 cube. In this case the four planar equatorial ligands are already in place. The oxo groups are inserted between the O^{2-} ions at the vertices of the PuO_8 cube that are not involved in the equatorial coordination, giving 1.95 Å oxygen-oxygen distances. Since these oxo groups are midway between two plutonium ions, they would form the same type of bond to the plutonium in the diagonally adjacent cell and what began as one plutonium(V) oxo complex automatically becomes a chain of them.

The fourth structure shows an alternative model, the conversion of two of the O^{2-} ions at opposite vertices of the PuO_8 cube into oxos so that the $\text{O}=\text{Pu}=\text{O}$ vector is normal to a [111] plane through the cube. In this case they are wholly within the unit cell of the central plutonium(V), avoiding the problems of bridging to neighboring plutonium ions and overlapping with other oxygen ions. However, creation of the equatorial plane requires that some of the O^{2-} ions from the other vertices must

Actinide ions in the higher oxidation states (V and VI) generally exist as trans dioxo (or actinyl) ions. Two oxygen atoms form strong covalent bonds with the actinide metal center to form a linear actinyl unit, $\text{O}=\text{An}=\text{O}$. All other ligands form bonds within an equatorial plane perpendicular to the linear $\text{O}=\text{An}=\text{O}$ unit. The equatorial plane typically contains four, five, or six other donor atoms as illustrated for (from top to bottom) $\text{PuO}_2\text{Cl}_4^{2-}$ (four chloride atoms), $\text{PuO}_2(\text{H}_2\text{O})_5^{2+}$ (five oxygen atoms from water molecules), and $\text{PuO}_2(\text{CO}_3)_3^{4-}$ (six oxygen atoms from carbonate ligands). In these examples the metal atoms are black, chlorides are blue, oxygens are red, and hydrogens are gray.

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ABSORPTION

be displaced into the [111] plane to create a set of equatorial ligands and the others displaced towards the adjacent cation holes. The formation of the plane now creates additional plutonium-oxygen distances of less than 1.9 Å, with asymmetric bridging. The collective effect here is that each new oxo group forces the formation of additional ones with neighboring plutonium atoms so that again a structural repeat chain develops.

The essential aspect of this plausible structural model is that it demonstrates, within the crystal and under the assumption that the coordination geometry is analogous to that in molecular complexes, that the formation of an oxo group on a particular plutonium ion forces the formation of additional oxo groups on neighboring plutonium ions. This sequence propagates through the crystal to form chains, filaments, or other types of clusters containing the plutonium(V)-oxo component.

This portion of the crystal structure of plutonium dioxide (PuO₂) illustrates the face-centered cubic arrangement of metal atoms in black, and three adjacent cubes of oxygen atoms (red). The figure on top shows the center cube occupied by one plutonium atom generating a central PuO₈ cube, while the two neighboring O₈ cubes are vacant. In the second figure, two interstitial oxygen atoms (light blue) are added into the vacancy positions. This model would give a Pu-O distance of 2.7 angstroms (Å), which is not consistent with the EXAFS data. The third figure illustrates the addition of two interstitial oxygen atoms (light blue) normal to a [110] plane the central PuO₈ cube with plutonium-oxygen (Pu-O) distances of 1.9 Å. In this case the four equatorial ligands (pink) are already in place. Since these new oxygen atoms bisect a cube edge, the new oxo groups are midway between two plutonium atoms, which results in the formation of a chain. The bottom figure shows the conversion of two oxygen atoms into short Pu=O groups along a body diagonal (normal to a [111] plane) of the central PuO₈ cube. This scenario requires distortion of the O₈ cube to create equatorial sites (pink).

This structural model assumes conservation of the plutonium sublattice, which follows from the diffraction results that show disorder but not the formation of a new phase. This result holds true for the EXAFS as well. Whereas, relative to the crystal, the oxygen shell forms a multisite distribution with the oxygen atoms organized around a set of specific plutonium-oxygen distances, there is no evidence for any new plutonium-plutonium distances or significant shift from the crystallographic plutonium-plutonium distance.

A complete description of all the detail embedded in the Fourier transform spectra is beyond the scope of this article; however, the prevailing thought is that the diminution in total amplitude in the Fourier transform spectra represents a material with coexisting crystalline and glassy characteristics. The poor coherence in the latter arrangement of atoms would result in a material with diminished diffraction characteristics so that the diffraction pattern displays only a single phase. The wide range of plutonium-oxygen near-neighbor distances is also consistent with a periodicity and the diffuse scattering from glasslike materials.

These off-stoichiometric plutonium dioxide subunit structures could exhibit some local order, but their small size and a periodic arrangement precludes efficient diffraction from them. The preponderance of oxo groups, as well as coordinated water, is suggested to therefore reside in domains of disordered material coexisting with more stoichiometric plutonium dioxide, thus resulting in a material that is heterogeneous on the nanometer scale.

Comparative behavior:

PuO_{2+x} versus UO_{2+x}

It is interesting to compare the local speciation and structural characteristics of PuO_{2+x} with the extensively studied UO_{2+x} system. We have also performed XAFS measurements on a series of UO_{2+x} samples,

where x varies from 0 to 0.20. The presence of multiple, coexisting, ordered phases correlated with the oxygen stoichiometry is well understood in this system, and specific structural models for these phases and the mechanism of oxygen addition have been developed.

Controlling the oxygen activity during calcination can produce exact oxygen stoichiometries in UO_{2+x} . Domains of the $\text{UO}_{2.25}/\text{U}_4\text{O}_9$ phase have been confirmed by x-ray diffraction with a slightly contracted lattice constant relative to that of the original UO_2 . This phase separation was easy to see and corroborated in XAFS data, where the high R features in the Fourier transform from the extended, ordered uranium dioxide structure all decrease linearly as the oxygen content increases.

A primary characteristic of extra lattice oxygen in both PuO_{2+x} and UO_{2+x} is the clear signature of oxo groups as x approaches 0.25. For both actinide oxides, the extra lattice oxygen is incorporated with the formation of oxo complexes analogous to the higher-valent molecular complexes. This incorporation is demonstrated by the Fourier transform spectra for the UO_{2+x} (analogous to those of PuO_{2+x}), which unequivocally show a resolved absorption feature at lower R comparable in amplitude to that of the O^{2-} contribution at high x (oxygen content) where the disorder has substantially lowered the amplitude in the Fourier transform spectra from the original oxygen shell.

For UO_{2+x} , the appearance of this new peak at low R is accompanied by the growth of other features at higher R that signify the simultaneous formation of oxygen shells with uranium-oxygen distances greater than 2.4 \AA and a multisite uranium-oxygen distribution. Curve fits demonstrate that this low R feature is well fit by an oxygen shell with a uranium-oxygen distance of about 1.75 \AA , significantly shorter than the oxo distance in PuO_{2+x} and more consistent with the oxo bond distances for uranium(VI).

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This result is significant in comparison to plutonium, where plutonium(V) is the preferred high-valence species resulting from oxygen or water oxidation of plutonium dioxide (see the previous and following articles). Another characteristic similar to PuO_{2+x} is that the total uranium amplitude also decreases with increasing x , implying the separation into a phase where the uranium sublattice retains the UO_2 structure and a separate phase that is more glasslike. The UO_{2+x} compounds, however, do not show the hydroxyl-water ligation common in the plutonium system and either have a much lower affinity for water or were well isolated from it during the entire course of their preparation.

Conclusion

From a critical interpretation of XAFS data, we have been able to identify specific, local coordination components for uranium and plutonium in the AnO_{2+x} solids. These components have included coordinated oxide ions, coordinated hydroxyls, and coordinated water. Furthermore, our data show that participation of repeat chain subunits of actinide ion coordinated to oxo subunits contribute greatly to the overall structural development of these materials.

Our research has shown that these high-valence actinide oxide complexes can be stabilized through the development of a complex heterogeneous environment on the nanometer-length scale. Much of this additional local structure possesses glasslike characteristics. More detailed information on the structures, additional characteristics of the reactivity, the behavior of other actinides, and the origins of these effects await further study.

How XAFS works

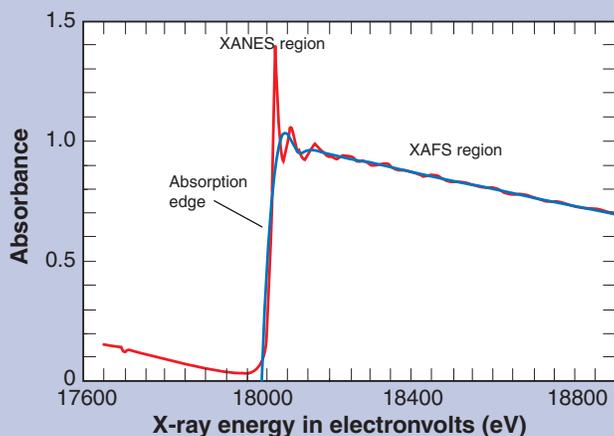
X-ray absorption fine structure (XAFS) spectroscopy is one of the most powerful tools we have for mapping local structure. In this technique, we probe a sample with x-rays that are tuned to the energy of a core electron shell in the element we wish to study. We monitor how many x-rays are absorbed as a function of their energy. If taken with sufficient accuracy, the spectrum exhibits small oscillations that are the result of the local environment's influence on the target element's basic absorption probability. From the spectrum, we can extract the distances between the absorber and its near-neighbor atoms, the number and type of those atoms, and the oxidation state of the absorbing element—all parameters that determine local structure. By selecting a different x-ray energy, we can obtain this information for any element in the sample.

An example of the absorption spectrum in the x-ray region is shown in the figure at right. The steplike rises occur where the x-ray energy has come into resonance with a core electron shell of one of the elements in the sample (plutonium in this example), exciting the electron into the continuum. Because of the shape of the spectral feature, the data are referred to as an absorption edge. For the most part the edges are widely separated and the target element is selected simply by scanning over an appropriate energy range. Following the edge, the absorbance decreases monotonically with increasing x-ray energy as the x-ray penetration depth becomes larger.

Fine structure is observed when the spectrum is expanded past a specific edge. The x-ray absorption near-edge structure (XANES) region occurs as peaks and shoulders over a 20 to 30 electronvolt-wide region immediately past the edge onset. The fine structure on the high-energy side of the edge that damps out over several hundred electronvolts is termed x-ray absorption fine structure (XAFS). This fine structure in both the XANES and the XAFS regions is well understood and enables XAFS to be applied to the determination of chemical speciation and local structure.

Beyond the edge region the XAFS fine structure occurs as a series of oscillations superimposed

upon what would be the smooth absorbance of the isolated atom. The origin of this fine structure arises from interference between the outgoing photoelectron wave and the portions of this wave backscattered off of neighboring atoms. The modulation of the interference condition with the change in x-ray energy results in oscillatory fine structure contributed by each neighboring atom.



The modulation in the XAFS is described by a single-scattering formulation that for the chemist contains several structurally significant metrical parameters. These parameters (noninclusive) include the number of neighbor atoms of the same atomic number at the same distance from the absorbing atom (i.e., a shell of neighbor atoms); a Z-dependent, per-atom backscattering amplitude function for that shell; the pair-wise Debye-Waller factor; and a phase-shift characteristic of the particular absorber-scatterer pair.

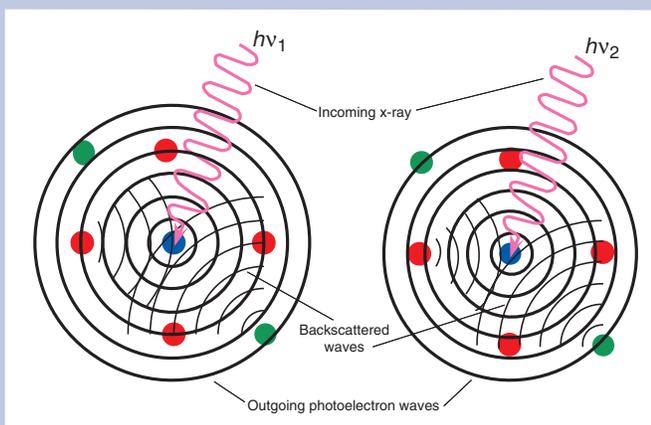
Mathematically, the scattering contributions can be summed over all of the shells and result in the composite XAFS spectrum. These metrical parameters are extracted from the data via nonlinear least-squares curve fits. A model consisting of a number of neighboring shells of atoms (supplemented by multiple scattering paths when necessary) is first devised. The XAFS is the sum of the individual waves from these shells, calculated from the single-scattering equation.

The source of the requisite phases and amplitudes for the fitting has evolved from the spectra of structurally analogous standard compounds to tabulated ones to very accurate *ab initio* calculations for arbitrarily arranged clusters of atoms that can be quite close to the final structure.

Phase shifts and amplitudes are unique to the different elements, with enough difference with increasing Z to allow the type of element to be identified to $\pm 3-4$ in principle. The structural parameters, e.g., R, N, and sometimes σ , are allowed to float until the least-squares difference between the data and the fit are minimized. Additional chemical information such as relationships between various parameters or shells or a permissible range for a parameter are introduced as constraints.

The view of XAFS as a superposition of sine waves dictates Fourier analysis, converting from $\chi(k)$ to $\chi(R)$ by Fourier transformation.

Since this converts each wave into a peak, $\chi(R)$ is related to the population-weighted average radial structure function around the absorber and the modulus does suggest a pair distribution around the absorber. For this reason, the Fourier transform representation ($\chi(R)$), and usually just the modulus, is most often used in figures despite most of the analysis actually occurring in k space ($\chi(k)$). The data are frequently shown as weighted spectra ($\chi^3(k)$) to (over)emphasize scattering contributions at longer distances.



Left: The x-ray absorption near-edge structure (XANES) shows a large peak, beyond which the x-ray absorption fine structure (XAFS) oscillations are readily observable against the spline polynomial (blue) that is used to approximate the smooth, atomic-like absorption above the edge.

Below: When x-ray energy E is absorbed by a central atom (blue), a photoelectron wave is propagated outward. This outgoing wave is backscattered off neighboring atoms (red and green) and interferes with itself at the origin. Left: Because of the ratio of the absorber-neighbor distance to the photoelectron wavelength, it is interfering constructively with respect to the first shell (red) and destructively with the second shell (green). Right: When x-ray energy $E + \Delta$ is absorbed by a central atom (blue), the photoelectron wavelength is changed and the interference conditions are altered. As the x-ray energy is scanned, the oscillation interference conditions result in oscillation in the absorption cross section, $\mu(k)$.

Predicting the behavior of stored excess plutonium

Using x-ray photoelectron spectroscopy to probe the surface chemistry of plutonium oxides exposed to water

This article was contributed by Doug Farr of the Nuclear Materials Technology Division, Roland Schulze of the Materials Science and Technology Division, and Mary P. Neu of the Chemistry Division.

Excess plutonium metal and residues from decades of production must be processed, stabilized, and packaged for safe, long-term storage. Current DOE guidelines require that excess plutonium be converted to the dioxide form, which is unusable in nuclear weapons, and packaged in sealed steel containers. Reactions at the interface between solid plutonium oxide particles and adsorbed gasses (which are either present initially or form during the vapor phase) play a dominant role in determining the pressure and atmosphere in these containers.

Understanding the chemistry at the solid vapor interface, particularly with respect to reactions with water vapor, is crucial for predicting the storage behavior of these materials. Safe storage of plutonium oxides requires minimal exposure to water vapor to limit chemically or radiolytically driven gas-generation reactions. Ultimately, the presence of water vapor may also affect container corrosion rates and limit container storage lifetimes.

Surface chemical reactions and their products also play a role in environmental plutonium behavior. For example, higher-valent plutonium species (V or VI) present at the surface of particulate matter may exhibit increased solubility. Determining the reactions at the solid water interface is important to understanding plutonium adsorption and desorption from minerals and ceramics.

X-ray photoelectron spectroscopy (XPS) is one of the main techniques used to characterize the surfaces of plutonium dioxide, plutonium hydroxide, and hyperstoichiometric plutonium oxide powders. XPS and the data obtained by it are only applicable to the outermost 2 to 5 nanometers (nm) of the surface. Because of its surface sensitivity, XPS complements the data obtained by x-ray absorption fine structure spectroscopy (XAFS), which are able to characterize the bulk of a sample.

The binding-energy values, distinctive line shapes, and peak widths obtained from well-characterized materials are used to interpret measured spectra of more-complex oxides, mineral-adsorbed species, and unknown forensic samples. In our study, we used reference spectra for the plutonium 4*f* and oxygen 1*s* levels of pure materials.

Previous articles in this issue of ARQ have either invoked the existence of a plutonium hydroxyl species or inferred its existence from EXAFS data. The data obtained from our experiments demonstrate its existence, provides quantitative estimates of amount, and further identify the valence of plutonium atoms in the surface region of the samples.

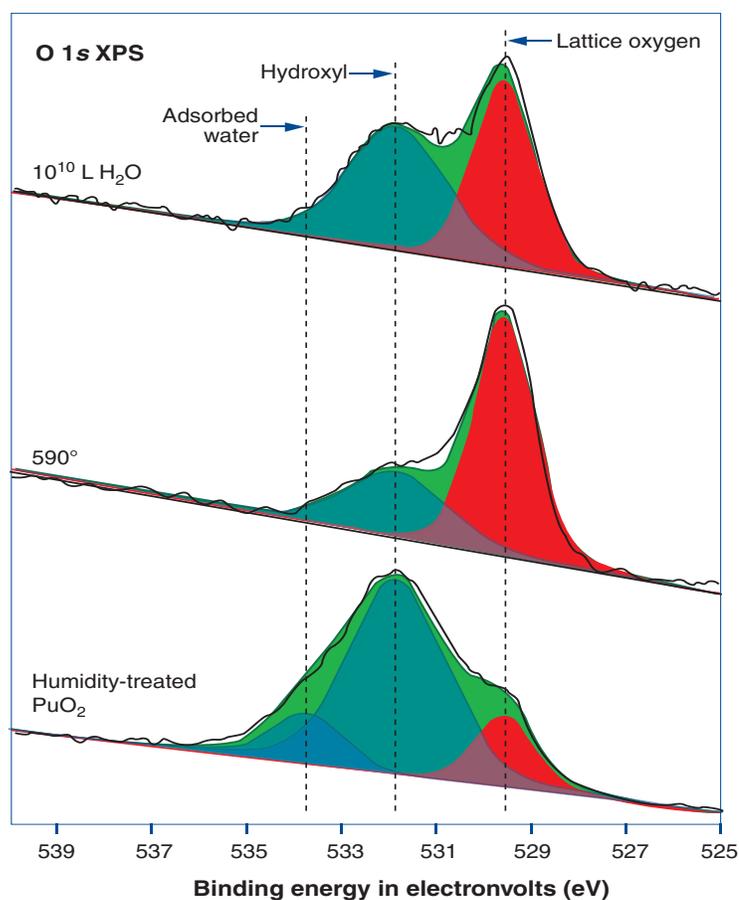
Our studies

Hyperstoichiometric oxides are plutonium oxide powders with the formula PuO_{2+x} . In our study, we analyzed samples formed by the reaction of high-fired plutonium dioxide with water vapor at elevated temperatures. The calculated composition for the material is $\text{PuO}_{2.26}$, based on the pressure of hydrogen (H_2) generated during the reaction at 300 degrees Celsius. The slightly expanded cubic lattice parameter for this material was 5.4022 angstroms (\AA), compared to 5.3975 \AA for stoichiometric plutonium dioxide. While the structure of PuO_{2+x} is unknown, possible structural models have been suggested in other articles in this issue.

The fraction of plutonium existing at higher oxidation states in the PuO_{2+x} material depends on how charges are balanced within various proposed model structures. One such structure, mentioned in the article on Page 9, places a hydroxyl ion at the face-centered cubic (fcc) body center and requires the oxidation of plutonium(IV) to plutonium(V). A more correct formula for this model is $\text{Pu}_4\text{O}_8\text{OH}$, consisting of three plutonium(IV) atoms and one plutonium(V) atom.

Other proposed models place an extra oxygen atom in various positions in the fcc lattice, including in the central octahedral site. Some charge transfer from the existing plutonium atoms must occur to balance the additional oxygen atom, but the details are still unknown. For most of the related materials that we have analyzed, plutonium was in the (IV) oxidation state, with the exception of PuO_2CO_3 , which was in the (VI) oxidation state. The value for x in PuO_{2+x} could be as high as 0.27, depending on preparation conditions, implying the presence of higher-valent plutonium in the material.

XPS is a convenient means of determining the valence and coordination chemistry at the surface of materials. One of the key technical advantages is that XPS can observe discrete differences in valence distributions in mixed-valent compounds in extended oxide structures. The time scale of the technique is applicable to processes occurring at a femtosecond (a quadrillionth of a second)

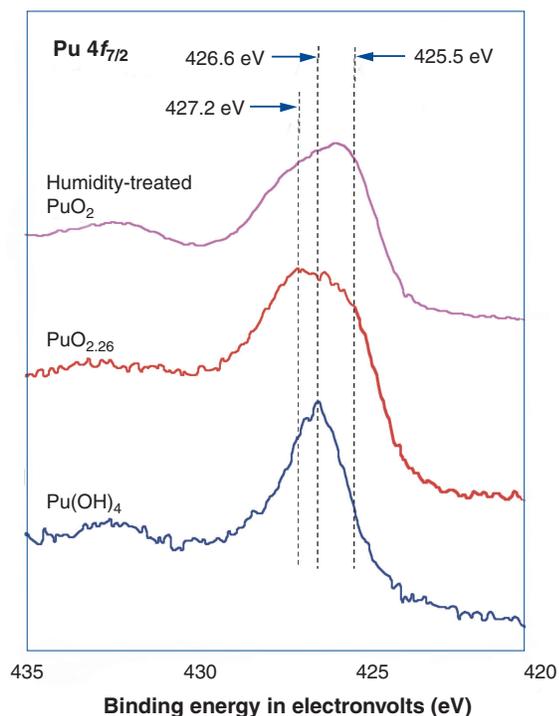


X-ray photoelectron spectroscopy (XPS) spectra from the oxygen 1s region of plutonium dioxide (PuO_2) following the treatments indicated.

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and unless the valence is truly shared among the actinide atoms in the solid structure, determining the oxidation states is possible. For example, XPS has unequivocally demonstrated that the unit cell of the uranium oxide U_3O_8 contains two uranium(VI) atoms and one uranium(IV) atom.

Equally important are the distinctions contained in the light elements such as carbon and oxygen. For oxygen-containing species, a very clear and significant distinction in measured binding energy enables both identification and quantification in the chemical bonding states. This distinction is shown in data obtained from a variety of plutonium dioxide solids following reactions with water vapor. We began by examining XPS data recorded over the core level oxygen 1s state,

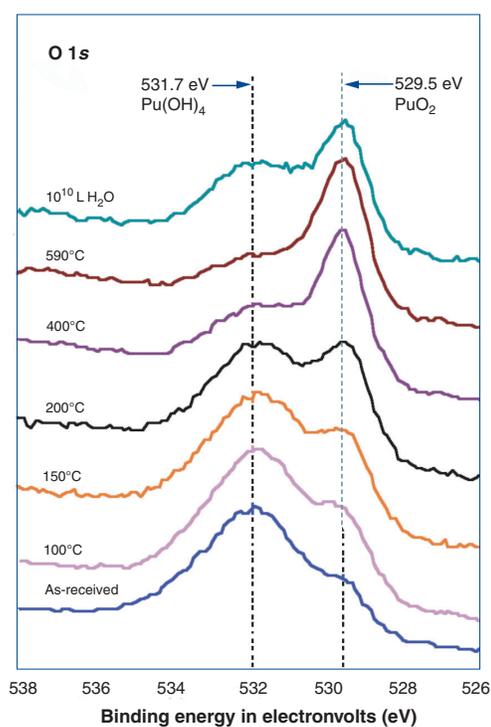
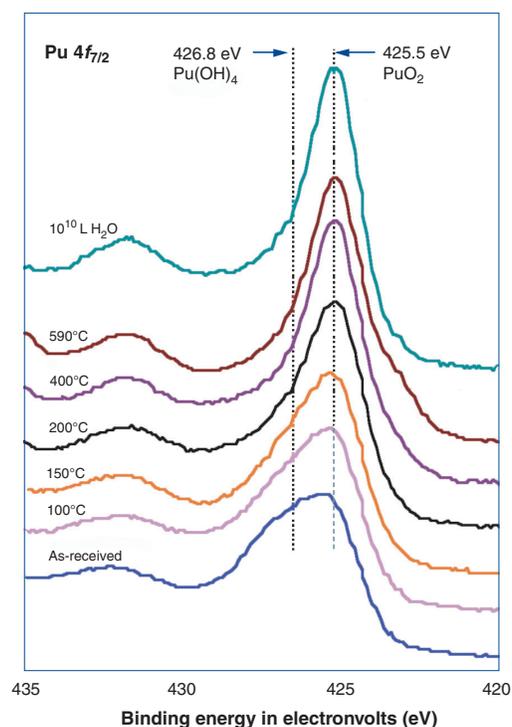


as shown in the figure on the previous page. Spectra obtained from these solids demonstrate a complex multiple-component line shape indicative of several chemical-bonding states of oxygen-containing entities.

From comparison to known reference compounds, the spectral assignments were ascribed to photoemission from oxygen present as lattice oxide ions, coordinated hydroxyl ions, and adsorbed water molecules. Following various treatment conditions, the distribution of different chemical states varied at the exposed plutonium oxide surface. However, in every example we studied the ubiquitous presence of surface hydroxyls was manifested.

Returning to the question of valence about the plutonium center in these various plutonium dioxide-treated samples, shown in the figure at left, shows XPS data centered about the dominant core-level line for plutonium, namely the $4f_{7/2}$ transition. An extensive discussion concerning XPS line shapes is beyond the scope of this article, but suffice it to say that the $PuO_{2.26}$ and PuO_2 samples treated with moisture both exhibited core-level shifts consistent with several chemical-bonding states present at values higher than nominally seen for plutonium(IV). In fact, the existence of plutonium(V) can be invoked based on comparison to reference data.

X-ray photoelectron spectroscopy (XPS) spectra for hydrated plutonium dioxide (PuO_2), $PuO_{2.26}$, and $Pu(OH)_4$ centered about the $4f_{7/2}$ transition.



These spectra show the plutonium $4f_{7/2}$ (left) and oxygen $1s$ (right) core levels for a plutonium dioxide powder in the as-received condition, through a series of thermal treatments, then followed by exposure to 10^{10} L H_2O . The plutonium $4f$ peaks narrow and become more bulk dioxide-like as the oxygen $1s$ dioxide peak grows with respect to the hydroxide intensity. Exposure to water vapor restores some surface hydroxides and eliminates the reduced plutonium oxide.

The thermal stability and reversibility of reactions involving water and plutonium oxides can be examined by monitoring the surface using XPS following various thermal excursions. Our samples were maintained in a rigorous vacuum following heating and were subject to an intrinsically reducing environment.

The figures above show stack plots of the plutonium $4f_{7/2}$ and oxygen $1s$ regions for a hydrated plutonium dioxide sample that was successively dehydrated by systematically heating the sample to progressively higher temperatures. Note the progressive shift and narrowing of the plutonium line back to a line shape close to that observed for plutonium dioxide at 400 degrees Celsius. For thermal treatments above 400 degrees Celsius, the appearance of a slightly lower binding-energy

state in the plutonium spectra is observed and is consistent with that seen for plutonium(III) as in the plutonium oxide form Pu_2O_3 .

The data show significant loss in the oxygen $1s$ features attributed to surface water and hydroxyls as well as the reappearance of the lattice oxygen chemical bonding states upon heating. The upper-most spectra were recorded following re-exposure of the plutonium sample to water; note the redevelopment of the feature hydroxyl along with the commensurate loss of the plutonium(III) entity.

Our research showed that surface hydroxylation occurred rapidly at very low water-vapor exposure, indicating that it is important to minimize the exposure to water vapor of samples intended for long-term storage. At room temperature, the hydroxylated layer is typically 3 nanometers (nm) thick.

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The surface hydroxides are tenacious and resist thermal decomposition up to 590 degrees Celsius. Important factors influencing surface chemistry include processing conditions (thermal treatment, in particular) and specific activity. Active sites for the reaction of water and other small molecules can be renewed by thermal energy or by effects of radiation. Although not specifically addressed in our study, we expect that other properties such as surface area, particle size, and particle morphology be parameters in describing reactivity in the study of the surface chemistry of plutonium oxides.

PuO_{2+x} shows evidence of extensive hydroxylation and spectroscopic features that are consistent with higher plutonium oxidation states, suggestive of plutonium(V). Curve fitting of the plutonium 4*f* levels indicates that about 10 percent of the plutonium is in this higher oxidation state. Plutonium oxide that has been exposed to air will display the complex surface chemistry demonstrated by the hyperstoichiometric plutonium oxide, including a small fraction of oxidation states greater than (IV).

Implications

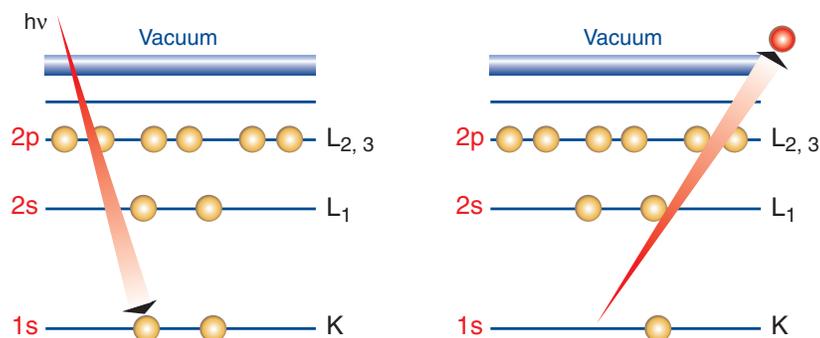
High-fired (heated to 900 degrees Celsius or higher for hours or longer) plutonium dioxide has been shown to be more highly ordered and more stoichiometric—that is, behaving more like plutonium(IV)—and so is more difficult to dissolve than low-fired material.

The higher degree of surface hydroxylation observed for PuO_{2+x} powders may effectively increase apparent plutonium solubility because hydrated plutonium dioxide ($\text{PuO}_2 \cdot \text{H}_2\text{O}$ or $\text{Pu}(\text{OH})_4$) has a higher free energy than stoichiometric high-fired plutonium dioxide and is therefore more soluble and prone to surface corrosion. Solubility studies of tetravalent actinides found greater solubility for amorphous plutonium dioxide than for crystalline plutonium dioxide in acidic solutions.

Our research has demonstrated several advantages inherent in surface analysis by XPS, including determining surface valency, quantifying stoichiometry, and in the case of oxygen species (or other light elements such as carbon), indirectly monitoring hydrogen-containing chemical states. Plutonium ions adsorbed from water on mineral surfaces is often observed by XPS in the (IV) state with peak positions and line shapes corresponding to those observed for the humid-air-exposed plutonium dioxide and $\text{Pu}(\text{OH})_4$ samples. The XPS spectra observed on air-exposed plutonium metal also share many of the same features—shake-up satellites characteristic of plutonium(IV) and broad peaks that indicate multiple chemical states for both plutonium and oxygen. Plutonium 4*f* binding energies and curve fitting of the oxygen 1*s* region for these samples have provided a more solid basis for understanding plutonium oxide surface chemistry.

How XPS works

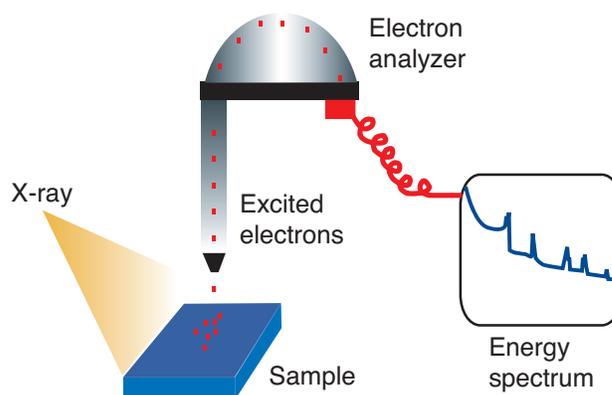
X-ray photoelectron spectroscopy (XPS) is a surface characterization technique that can analyze a sample to a depth of 2 to 5 nanometers (nm). Kai Siegbahn, who won the Nobel Prize in physics in 1981 for his research, developed XPS in the 1960s. XPS reveals which chemical elements are present at the surface and the nature of the chemical bond that exists between these elements. It can detect all of the elements except hydrogen and helium.



XPS is conducted in ultrahigh vacuum (UHV) conditions, around 10^{-9} millibar (mbar). Atmospheric pressure is about 1 bar, which means that the number of atoms of gas in a UHV chamber is one-trillionth that of air per unit of volume. The ambient atmosphere that a

sample is exposed to can change its properties. For example, at a pressure of 10^{-6} mbar, background gas constituents (O_2 , H_2O , etc.) can react with the surface of a sample in several seconds. Even under optimal instrumental conditions this is too little time in which to conduct an experiment. However, at UHV pressures it takes hours before a sample significantly degrades, thus enabling accurate surface interrogation using XPS.

Irradiating a sample with x-rays of sufficient energy results in electrons in specific bound states to be excited. In a typical XPS experiment, sufficient energy is input to break the photoelectron away from the nuclear attraction force of an element. Two key features are derived from XPS data. The first is that even photoejected electrons from core levels have slight shifts depending on the outer valence configuration of the material examined. The second



Photoemission principle: When an x-ray (red arrow) bombards a sample (left), some electrons (yellow spheres) become excited enough to escape the atom (right).

How XPS WORKS

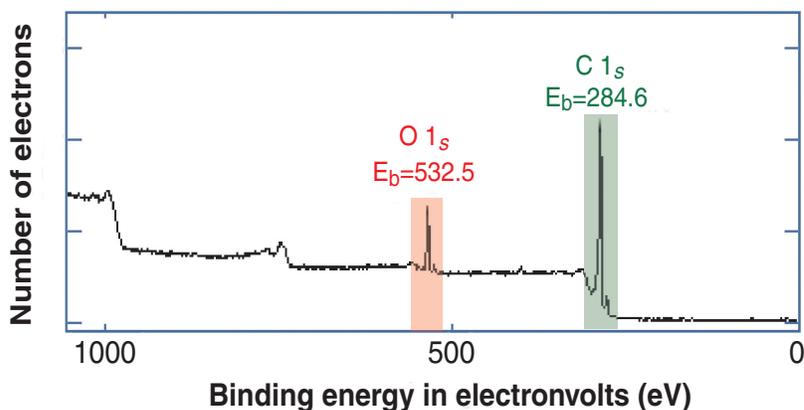
is that the specific energy of an elemental core level transition occurs at a specific binding energy that can uniquely identify (and in favorable cases quantify) the element.

In a typical XPS spectrum some of the photo-ejected electrons inelastically scatter through the sample enroute to the surface, while others undergo prompt emission and suffer no energy loss in escaping the surface and into the surrounding vacuum. Once these photo-ejected electrons are in the vacuum, they are collected by an electron analyzer that measures their kinetic energy. An electron energy analyzer produces an energy spectrum of intensity (number of photo-ejected electrons versus time) versus binding energy (the energy the electrons had before they left the atom). Each prominent energy peak on the spectrum corresponds to a specific element. In the spectrum below, there is a peak at 284.6 electronvolts (eV), which corresponds to carbon, and a peak at 532.5 eV, which corresponds to oxygen; therefore, this sample contains carbon (C) and oxygen (O).

Besides identifying elements in the specimen, the intensity of the peaks can also tell how much of each element is in the sample. Each peak area is proportional to the number of atoms present in each element. The specimen's chemical composition is obtained by calculating the respective contribution of each peak area. By applying relative sensitivity factors and appropriately integrating peak areas, it can be determined that the sample below is 25 percent oxygen and 75 percent carbon.

By studying the energy of the carbon peak, it can also be determined if the surface of this material corresponds to a C–O single bond (ethers, alcohols) or a much stronger C=O double bond (carboxylates, ketones). Core level shifts are important in determining valence states in metals, transition metal oxides, and actinide materials.

—Information for this article was taken from Thermo Electron Corp.'s website on XPS (www.lasurface.com)



Actinide Research Quarterly
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National Laboratory

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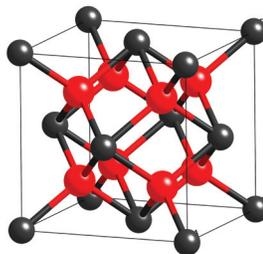
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LALP-04-060

